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Preface

The present thesis, entitled "Source zone remediation by zero valent iron technologies", has been submitted as part of the requirement for obtaining a PhD degree from the Technical University of Denmark (DTU). The research was primarily conducted at the Department of Environmental Engineering at DTU from September 2006 to February 2011; an external stay at the Center for Contaminant Hydrology, Colorado State University was included (June to September 2007). The research was carried out under the supervision of Professor Peter Kjeldsen (primary supervisor) and Professor Anders Baun (co-supervisor). The funding was primarily obtained through a PhD scholarship from DTU, while the Capital Region of Denmark provided funding for the extensive field work.

The thesis comprises a summary and four papers prepared for scientific journals; at the time of writing one of the papers is published, while the remaining three are presented as manuscripts:

I. Grieger, K.D., Fjordbøge, A., Hartmann, N.B., Eriksson, E., Bjerg, P.L., Baun, A. (2010). Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for *in situ* remediation: Risk mitigation or trade-off? J. Contam. Hydrol. 118, 165-183.

II. Fjordbøge, A.S., Olson, M.R., Sale, T.C., Kjeldsen, P. (2011). ZVI-Clay soil mixing – an innovative remediation technology for chlorinated solvents source zones. Manuscript.

III. Fjordbøge, A.S., Riis, C., Christensen, A.G., Kjeldsen, P. (2011). ZVI-Clay remediation of a chlorinated solvent source zone, Skuldelev, Denmark: 1. Site description and source mass reduction. Manuscript to J. Contam. Hydrol.

VI. Fjordbøge, A.S., Lange, I.V., Bjerg, P.L., Binning, P.J., Riis, C., Kjeldsen, P. (2011). ZVI Clay remediation of a chlorinated solvent source zone, Skuldelev, Denmark: 2. Groundwater mass discharge reduction. Manuscript to J. Contam. Hydrol.

In the thesis, these papers are referred to by the author name and the Roman numeral accentuated in bold (e.g., Fjordbøge et al., **II**).

The papers are not included in this www-version but can be obtained from the Library at DTU Environment, Department of Environmental Engineering, Technical University of Denmark, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark (library@env.dtu.dk).

During the PhD study I have presented my research orally several times; the presentations have primarily been given at the eight national and international conferences I have attended. The conference attendance has also resulted in a total of seven papers in the conference proceedings. In addition, five technical reports and some technical notes for the Danish EPA and the Capital Region of Denmark have been prepared in cooperation with two Danish consultant companies. These additional activities are not part of the thesis; however, as the work has been related to the overall topic of the thesis some of it will be referred to.

Kgs. Lyngby, March 2011
Annika S. Fjordbøge

Acknowledgement

There are a number of people I would like to thank for their help throughout my PhD project:

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- My family and friends. Especially, my parents, *Lene* and *Jørgen*, for their unconditional love and encouragement. Last but not least my warmest gratitude to my husband, *Patrick*, my always patient and optimistic counterpart. Thank you for the generous support and for always insisting that everything is going to be all right.

I have greatly appreciated all of these professional and personal contributions during my years as a PhD student.

"The true delight is in the finding out rather than in the knowing" – Isaac Asimov

Abstract

Chlorinated solvents have been widely used as industrial solvents. Decades of extensive use have resulted in the contamination of an estimated 800,000 sites in the western world alone. A medium to high risk of problems related to dense non-aqueous phase liquids (DNAPLs) has been assessed to exist at a fifth of these contaminated sites. These source zones pose a serious threat to soil and groundwater quality. Remediation of the heterogeneous source zones is challenging due to irregular downwards migration patterns in the subsurface, low aqueous solubility and matrix diffusion.

To protect the soil and groundwater resources from long-term deterioration, the development of *in situ* technologies suitable for remediation of DNAPL is warranted. Currently, an array of aggressive *in situ* remediation technologies remediation exists. These technologies may be suitable under various site specific conditions; however, most of them are limited by subsurface heterogeneities and/or the risk of inadvertent DNAPL displacement during field application.

This thesis presents the results of an investigation of the potential for remediation of chlorinated solvent source zones by emerging zero valent iron (ZVI) based technologies. These *in situ* remediation technologies include the injection of nanoscale ZVI (nZVI) particles and the addition of ZVI and clay through soil mixing (ZVI-Clay soil mixing). The investigation of the nZVI technology is based on an elaborate literature review, while the investigation of the ZVI-Clay soil mixing technology is based on experimental data from bench-scale studies and field applications. Generally, both technologies are efficient at degrading chlorinated solvents with only a minor production of persistent chlorinated intermediates. To date, the nZVI technology has been applied at around 40 contaminated sites, while the ZVI-Clay soil mixing technology has been applied in full-scale at 9 contaminated sites. Scarce performance data exist for most of these sites; this limits the assessment of the potential for source mass depletion and risk mitigation at down-gradient receptors by the ZVI technologies.

When investigating the nZVI technology specifically, this technology utilizes the decreased particle size (<200 nm) and increased specific surface area (~30 m^2/g) of the nanoparticles. These properties enhance the reactivity of ZVI and the deliverability through injection. Various nZVI products with diverse properties exist; the properties are altered by applying surface modifications that increase the reactivity of nZVI, the mobility of nZVI, and affinity for the DNAPL. These properties are continuously optimized to improve the remedial efficiency of the nZVI technology. The nZVI technology is efficient at degrading solute contaminants in the groundwater plume, while a rebound in groundwater concentrations has been observed when applied to source zones. The nZVI

technology relies on injection for delivery of the highly reactive particles; this makes the technology vulnerable to subsurface heterogeneities and the presence of DNAPL. Several reinjections are likely to be required to achieve efficient source mass depletion. Presently, the subsurface fate and the toxicity of existing nZVI particles are generally unknown aspects of the technology. Few toxicological studies exist, and the fate of nZVI is primarily based on idealized bench-scale studies. No severe apparent risks involving nZVI application has been identified; however, due to the uncertainty of the key metrics in risk assessment (persistency, bioaccumulation and toxicity) the nZVI risk is hard to classify. The risks associated with nZVI application are expected to change as the characteristics of nZVI are optimized.

The ZVI-Clay soil mixing technology was found to be efficient for source mass depletion in the presence of free phase DNAPL. Removal efficiencies of around two orders of magnitude were generally achievable with one year after the implementation. Only limited horizontal homogenization was facilitated by the technology; this may be used in the remedial design for a division into several specific subzones with specific remedial objectives. Considerable vertical homogenization of ZVI, the encountered geological layers, and the contaminants was achieved. The most homogeneous conditions were achieved by auger mixing with ZVI added to the drilling fluid. The swelling properties of bentonite clay produced a superior drilling fluid, larger hydraulic conductivity reduction and better DNAPL emulsification. The reduced hydraulic conductivity of the soil mixed source zone resulted in an immediate reduction of the down-gradient contaminant mass discharge. The later mass discharge development depended on: the source mass depletion rate, the site specific conditions, and the changes in source mass accessibility induced by soil mixing. The main limitations of the technology are the heavy soil mixing equipment (site accessibility and mobilization cost for small sites) and the reduced post-mixing soil strength (site restoration and future use).

To conclude, the investigated ZVI technologies can be viable alternatives to other *in situ* remediation technologies. The nZVI technology can primarily be used for remediation of the contaminated plume or homogeneous source zones without free phase DNAPL. The technological limitations are similar to other injection based technologies (e.g., *in situ* chemical oxidation or *in situ* flushing with cosolvents or surfactants). The ZVI-Clay soil mixing technology has shown high removal efficiencies at heterogeneous source zones with free phase DNAPL. Hence, the ZVI-Clay soil mixing technology can potential be used for remediation at some of the several thousand sites affected by DNAPL contamination.

Dansk sammenfatning

Klorerede opløsningsmidler har været hyppigt brugt til industrielle formål. Den omfattende brug igennem flere årtier har resulteret i forurening af omkring 800,000 grunde alene i den vestlige verden. Det er vurderet, at der er en middel til høj risiko for DNAPL (tung ikke blandbare væske) relaterede problemer på en femtedel af disse forurenede grunde. Disse kildeområder udgør en seriøs trussel mod jord- og grundvandskvaliteten. Oprensning af kildeområder i heterogene grundvandsmagasiner er udfordrende pga. den irregulære spredning af DNAPL, den lave vandopløselighed og diffusion ind i lavpermeable lag.

For at beskytte jord- og grundvandsressourcerne fra en langvarig forringelse er det nødvendigt at udvikle *in situ* afværgeteknologier til oprensning af DNAPL kildeområder. Der eksisterede allerede en række *in situ* afværgeteknologier. Disse teknologier kan være egnede under forskellige feltforhold, men de fleste af dem har begrænsninger relateret til heterogene forhold i grundvandsmagasinet og/eller en risiko for en utilsigtet spredning af DNAPL.

I denne afhandling er muligheden for at bruge de nyeste afværgeteknologier baseret på nul valent jern til at oprense DNAPL kildeområder med klorerede opløsningsmidler blevet undersøgt. Disse nye afværgeteknologier inkluderer injektion af nanopartikler bestående af nul valent jern (nZVI) og tilsætningen af nul valent jern og ler via en mekanisk opblanding af jorden (ZVI-Clay soil mixing). Undersøgelsen af nZVI er baseret på et dybdegående litteratur studie, mens undersøgelsen af ZVI-Clay soil mixing er baseret på eksperimentelle resultater fra laboratoriet og felten. Begge teknologier er generelt effektive til at nedbryde klorerede opløsningsmidler med kun en mindre produktion af langsomt nedbrydelige forbindelser. Indtil nu er nZVI blevet anvendt på omkring 40 forurenede grunde, mens ZVI-Clay soil mixing er blevet anvendt til oprensning af 9 forurenede grunde. Der er afrapporteret en begrænset mængde data angående virkningsgraden er teknologierne. Dette begrænser vurderingen af egnetheden af de nul valent jern baserede teknologier til oprensning af forurenede grunde og til at afhjælpe nedstrøms risici.

Når man undersøger nZVI specifikt, så udnytter denne teknologi den begrænsede størrelse (<200 nm) og det høje specifikke overfladeareal (ca. 30 m^2/g) af nanopartiklerne. Disse egenskaber øger reaktiviteten af nul valent jern, samt gør det muligt at levere partiklerne til grundvandsmagasinet via injektion. Der findes en række nZVI produkter med forskellige egenskaber. De forskelligartede egenskaber stammer fra modifikationer af overfladen på nZVI. Dette kan øge nanopartiklernes reaktivitet og mobilitet, samt øge affiniteten for DNAPL. Alle disse egenskaber optimeres løbende for at forbedre teknologiens virkningsgrad. Opløste forbindelser i grundvandsfanen kan effektivt nedbrydes med nZVI. Ved oprensning i kildeområder er der blevet observeret stigninger i

grundvandskoncentrationerne efter afslutningen af oprensningen. Teknologien er baseret på injektion af de reaktive nanopartikler og er dermed sårbar overfor heterogeniteten i grundvandsmagasinet og forekomsten af DNAPL. Gentagne injektioner vil være påkrævet for at opnå effektiv nedbrydning af forureningsmassen i et kildeområde. På nuværende tidspunkt er det i høj grad ukendt hvad der sker med nZVI efter injektionen. Dette drejer sig både om hvordan partiklen udvikler sig i grundvandsmagasinet, indtil videre er dette kun kendt under ideelle laboratorieforhold, og om hvor toksiske partiklerne er, indtil videre er der kun udført få toksicitetstest. Der er ikke blevet identificeret nogle alvorlige risici ved at anvende nZVI, men toksiciteten er endnu svær at klassificere pga. det begrænsede vidensniveau. Risici i forbindelse med teknologien forventes at ændres som egenskaberne af nZVI optimeres.

Effektiv oprensning af DNAPL kildeområder er blevet opnået med ZVI-Clay soil mixing. Ét år efter igangsættelsen af afværgeprojekterne var der, generelt set, sket en reduktion af forureningskoncentrationerne i omegnen af to størrelsesordener. Teknologien opnåede en meget begrænset horisontal homogenisering. Dette er ikke en begrænsning af teknologien, men kan derimod bruges i designet til at inddele kildeområdet i flere underområder med forskellige målsætninger. Der blev opnået en bedre vertikal homogenisering af nul valent jern, påtrufne geologiske lag og de forurenende forbindelser. Den bedste homogenisering blev opnået med et sneglebor, hvor nul valent jern blev tilsat sammen med boremudderet. Bentonit er bedst egnet til fremstilling af boremudder pga. lerets evne til at kvælde. Denne egenskab giver bedre moremudder egenskaber, større nedsættelse af den hydrauliske ledningsevne og bedre emulgering af DNAPL. Den nedsatte hydrauliske ledningsevne i kildeområdet resulterer i en umiddelbar reducering af forureningsfluxen nedstrøms fra området. Den senere udvikling af forureningsfluxen afhænger af: hvor hurtigt forureningen i kilden nedbrydes, de specifikke feltforhold, og eventuelle ændringer i tilgængeligheden af kildeforureningen pga. opblandingsprocessen. De største begrænsninger for teknologien er det tunge maskineri der anvendes til opblandingen (tilgængelighed til området og mobiliseringsomkostninger) og jordens reducerede styrke efter opblandingen (fremtidig brug af lokaliteten).

Opsummerer man, betyder dette, at begge de undersøgte teknologier kan være mulige alternativer til andre etablerede afværgeteknologier. Teknologien med nZVI kan hovedsageligt anvendes til at oprense forurenede grundvandsfaner eller homogene kildeområder uden kraftig DNAPL forurening. Teknologien har de samme begrænsninger som andre injektionsteknologier (f.eks. *in situ* kemisk oxidation). ZVI-Clay soil mixing har opnået høje oprensningsgrader for DNAPL kildeområder i heterogene grundvandsmagasiner. Dermed kan ZVI-Clay soil mixing potentielt anvendes på nogle af de mange tusinde forurenede grunde med DNAPL relaterede problemer.

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1 Introduction

1.1 Background and motivation

Contamination with chlorinated solvents in the form of persistent immiscible dense non-aqueous phase liquids (DNAPLs) is one of the greatest remedial challenges at old industrial sites. Decades of extensive use has placed the chlorinated solvents high on the list of the most commonly found contaminants (Doherty, 2000a; US EPA, 2004). Consequently, it is estimated that thousands of sites around the world are in need of remediation. In the United States the estimate is around 300,000 sites (US EPA, 2004), while the estimate for Europe is around 500,000 sites (EC, 2006). On a local scale, 24,000 Danish sites are reported to be contaminated or potentially contaminated (DK EPA, 2010a). A high fraction (15-20 %) of the contaminated sites is assessed to have a medium to high risk of problems related to the presence of DNAPL (US EPA, 2004). The development of technologies suitable for remediation of these source zones is thereby warranted.

The contaminated source zones in the saturated subsurface pose a threat to soil and groundwater quality. The long-term deterioration of soil and groundwater quality and the subsequent risk to down-gradient receptors emphasize the need for efficient remediation technologies to mitigate these problems. Currently, an array of aggressive *in situ* remediation technologies exists. These technologies are applicable under various site conditions, but the presence of DNAPL in the subsurface limits the potential for complete source mass depletion (Sale & McWhorter, 2001; Stroo et al., 2003). To accommodate the technological challenges of source zone remediation, new and existing technologies are continuously being developed.

At many source zones, the reduction of contaminants to strict regulatory maximum concentration levels is often not realistic within a reasonable time frame. For partial source mass depletion to be feasible, more pragmatic regulatory approaches are needed. The determination of mass discharge from the source zone to the down-gradient receptors has been suggested as a more risk-based approach (e.g., Basu et al., 2006; Einarson & Mackay, 2001; Freeze & McWhorter, 1997; Jawitz et al., 2005; Soga et al., 2004; Stroo et al., 2003; Troldborg et al., 2008). Hence, the development of new *in situ* remediation technologies should focus on both the source mass depletion and the related down-gradient mass discharge.

Zero valent iron (ZVI) has been used in permeable reactive barriers for passive *in situ* remediation of contaminated groundwater plumes (e.g., Henderson & Demond, 2007; Phillips et al., 2010). The technology was pioneered by the University of Waterloo in the 1990s (Gillham & O'Hannesin, 1994; O'Hannesin

& Gillham, 1998). The ability of the ZVI technology to reduce chlorinated solvents has made it a target for further development. Emerging *in situ* remediation technologies strive to exploit the ZVI reactivity for source zone remediation. Enhanced source mass depletion can be achieved through the use of either a more reactive ZVI agent or a more efficient method of delivery. The emergence of nanotechnology has introduced an opportunity to engineer highly reactive ZVI nanoparticles (nZVI) for field applications (e.g., Elliott & Zhang, 2001; Elsner et al., 2010; Greiger et al., **I**; He et al., 2010; Henn & Waddill, 2006; Quinn et al., 2005). However, as an injection based technology the efficiency of nZVI remediation is limited by subsurface heterogeneities. The delivery of reactive agents to the heterogeneous subsurface and the following contact with the contaminants has been identified as a main challenge for *in situ* remediation technologies (Nyer & Page, 2004). To overcome some of the challenges with subsurface heterogeneities, the use of soil mixing as a delivery method for ZVI is under development (e.g., Fjordbøge et al., **II**, **III**; Wadley et al., 2005). The research advances for the ZVI technologies have so far primarily been achieved in bench-scale studies; few reports are available on field applications. Hence, further research into the development of the aggressive *in situ* ZVI technologies for source zone remediation is warranted.

1.2 Research objectives

The overall aim of this thesis was to investigate the potential of *in situ* source zone remediation of chlorinated solvents by ZVI technologies. Specifically, the objectives were:

- To review the current level of field applications of the nZVI technology. This included the identification of the likely fate, hazards and benefits of the nZVI particles (Greiger et al., **I**).

- To determine the efficiency of ZVI-Clay soil mixing for source mass depletion of chlorinated solvents. This included an investigation of soil mixing as a delivery method; specifically, the effects of clay addition, the vertical and horizontal homogenization, and the limitations related to the technology (Fjordbøge et al., **II**, **III**).

- To investigate the down-gradient effects of ZVI-Clay soil mixing. This included the changes in mass discharge, the factors affecting these changes, and the relationship between the mass discharge and the source mass depletion (Fjordbøge et al., **IV**).

The investigation of the nZVI technology has been based on a review of relevant literature, while the investigation of the ZVI-Clay soil mixing technology has been based on novel experimental data from bench-scale studies and the field applications.

1.3 Outline for the thesis

The thesis has been structured as described in the following. Chapter 2 and 3 are background chapters that provide the context for development of the new remediation technologies. Chapter 2 provides an overview of the use, characteristics and spreading of chlorinated solvents (DNAPL) in the subsurface. Chapter 3 provides an overview of established *in situ* remediation technologies. Chapter 3 also includes an overview of the basic processes for ZVI-mediated degradation of chlorinated solvents. Chapter 4 and 5 present the emerging ZVI technologies for *in situ* source zone remediation. Chapter 4 focuses on the injection of nZVI, which include the use of nZVI for source remediation, the environmental fate of nZVI, and the possible risks of applying the nanoparticles to the subsurface. Chapter 5 focuses on ZVI-Clay soil mixing, which includes the source mass depletion, the soil mixing process, and the down-gradient effects on mass discharge. Chapter 6 concludes on the main outcomes of the thesis, while chapter 7 outlines some of the areas to which future research should be directed. Finally, the four scientific papers, that this thesis is comprised of, are included in chapter 9.

2 Chlorinated solvents in the subsurface

The specific characteristics of the chlorinated solvents make *in situ* remediation of the contaminants in the subsurface challenging. The following chapter will outline some of the aspects related to source zone development and the relationship with the development of the down-gradient groundwater plume. The understanding of these aspects is important in the development of efficient *in situ* remediation technologies.

2.1 Characteristics and use of chlorinated solvents

Chlorinated aliphatics have been widely used in the industry as dry-cleaning and metal-degreasing solvents. Carbon tetrachloride (CT) was among the first chlorinated solvents to be used extensively by the industry. Later, tetrachloroethene (PCE) became the predominant solvent for dry cleaning, while trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) primarily were used for metal degreasing. The use of the chlorinated solvents peaked in the 1970s and then decrease as the industry became more efficient and the environmental legislation evolved. Due to the widespread industrial application of chlorinated solvents, these are among the most common contaminants found at old industrial sites (Doherty, 2000a, 2000b).

According to the International Agency for Research on Cancer (IARC) several chlorinated solvents and their degradation products are carcinogenic or possible carcinogens (IARC, 2010). In addition, chlorinated solvents are generally denser than water, immiscible with water, and relatively volatile (Table 2.1). Hence chlorinated solvents can pose a risk to the environment and human health by deteriorating the quality of air, water and soil.

Table 2.1. Properties of selected chlorinated solvents and their degradation products.

Compound	**Density** [1] *[g/cm^3]*	**Solubility**[1] *[mg/L]*	**Henry's constant**[1] *[-]*	**Carcinogenic** *[IARC Class]*[2]	**Quality criteria**[2] *[µg/L]; [mg/kg]*	
PCE	1.63	240	0.7	2A	1;	5
TCE	1.47	1400	0.4	2A	1;	5
Cis-DCE	1.27	3500	0.2	-	1;	85
Vinyl chloride (VC)	0.92	2800	1.1	1	0.2;	0.4
CT	1.58	780	1.2	2B	1;	5
Chloroform (CF)	1.50	8700	0.2	2B	1;	50
1,1,1-TCA	1.35	1300	0.7	3	1;	200

1At 25 °C (Kjeldsen & Christensen, 1996).
[2]1: Carcinogenic; 2A: Probably carcinogenic; 2B: Possibly carcinogenic; 3: Not classifiable.
[3]Groundwater quality criteria and soil quality criteria from the Danish EPA (DK EPA, 2010b).

2.2 Source zone development

A source zone comprising residual and free phase DNAPL will develop after the release of a sizeable amount of chlorinated solvents to the subsurface. The specific characteristics of the chlorinated solvents (Table 2.1) control the spreading pattern of DNAPL in the subsurface. The low solubility and high density of the chlorinated solvents allow the DNAPL to migrate downwards, while the concurrent partitioning processes (e.g., dissolution, volatilization, and sorption) result in further spreading throughout the subsurface.

The distribution of DNAPL in the subsurface is generally highly irregular; the distribution depends on even small geological heterogeneities that deflect the overall downwards migration pathway (Poulsen & Kueper, 1992; Kueper et al., 1993). On the way though the subsurface, trace amounts are retained in the porous media by the capillary forces, and lateral pools accumulate on low-permeable layers (Figure 2.1a). The DNAPL accumulates until the capillary entry pressure of the encountered layer is overcome or a more permeable vertical pathway is encountered (Kueper et al., 1993; Parker et al., 1997). Aging of the source zone changes the distribution of DNAPL (Figure 2.1b). Over time the accessible DNAPL dissolves, while the less accessible DNAPL persists as a long-term source of down-gradient contamination (Parker et al., 2003). The contaminants can diffuse from the DNAPL pool into the low-permeable layer. The matrix diffusion can cause back-diffusion and continuous groundwater contamination following the depletion of the lateral DNAPL pools; this can also be observed as a rebound in groundwater concentrations after *in situ* remediation (Chapman & Parker, 2005; Liu & Ball, 2002; VanderKwaak & Sudicky, 1996).

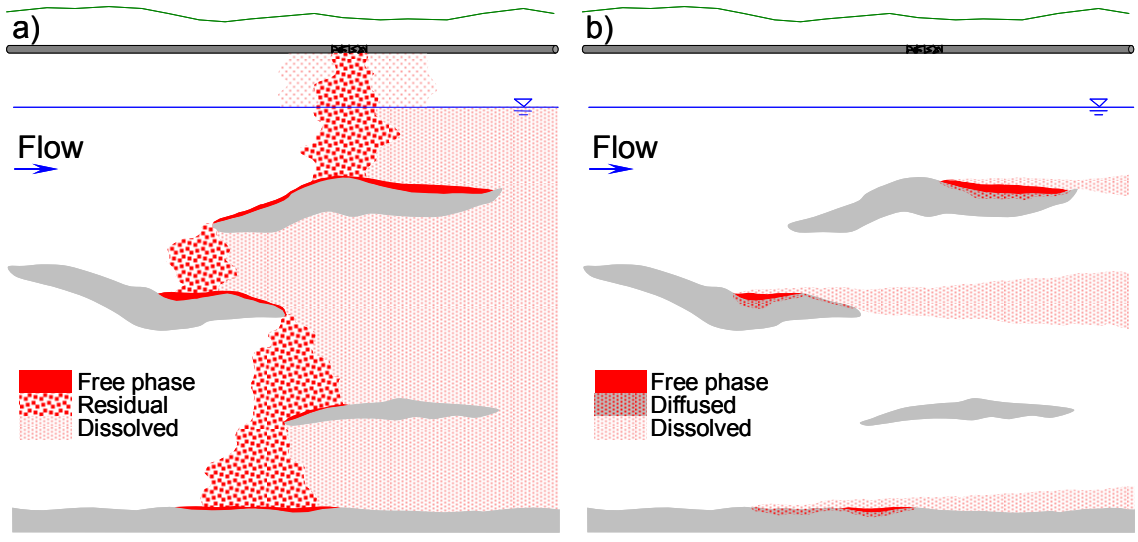

Figure 2.1. Conceptual model of the spreading of DNAPL in a heterogeneous subsurface, including free phase DNAPL pools, residual DNAPL, dissolved contaminant, and matrix diffusion. Two different stages of the distribution development are illustrated, namely: a) the early source development; and b) the aging source zone where lateral pools are left (based on Parker et al., 2003).

2.3 Down-gradient plume development

The groundwater quality criteria for chlorinated solvents are often strict. Even with the low solubility of most chlorinated solvents (Table 2.1) down-gradient compliance with the quality criteria can be challenging. Mass discharge from the source zone is the driver for the down-gradient development of the contaminated plume. This makes the mass discharge through a down-gradient control plane a suitable metric for describing the severity of the contamination; mass discharge is also useful for assessment of any changes in the risk at the down-gradient receptors after the application of an *in situ* remediation technology (e.g., Basu et al., 2006; Brooks et al., 2008; Einarson & Mackay, 2001; Guilbeault et al., 2005; Jawitz et al., 2005; Soga et al., 2004; Troldborg et al., 2008). The mass discharge from a source zone through a down-gradient control plane perpendicular to the flow direction can be described as (e.g., Basu et al., 2006):

$$M_D = \int_A iKC\, dA = \int_A qC\, dA \qquad \text{(Eq. 2.1)}$$

where M_D [M T^{-1}] is the mass discharge, i is the hydraulic gradient [dimensionless], K is the hydraulic conductivity [L T^{-1}], C is the solute concentration [M L^{-3}], q is the Darcy velocity [L T^{-1}], and A is the cross section area of the control plane [L^2].

2.3.1 Mass discharge determination by multilevel sampling

The accuracy for determination of mass discharge depends on the density of sampling points at the down-gradient control plane. A division of the control plane into subareas with varying chemical and hydraulic properties can be done. When the control plan is divided into n subareas, the mass discharge can be calculated as the sum of mass discharge through all the subareas (Guilbeault et al., 2005):

$$M_D = \sum_{i=1}^{n} q_i C_i A_i \qquad \text{(Eq. 2.2)}$$

The variation between the mass discharge obtained with sparse data from conventional monitoring wells and the mass discharge obtained with data from a denser multilevel sampling network can be considerable (Figure 2.2).

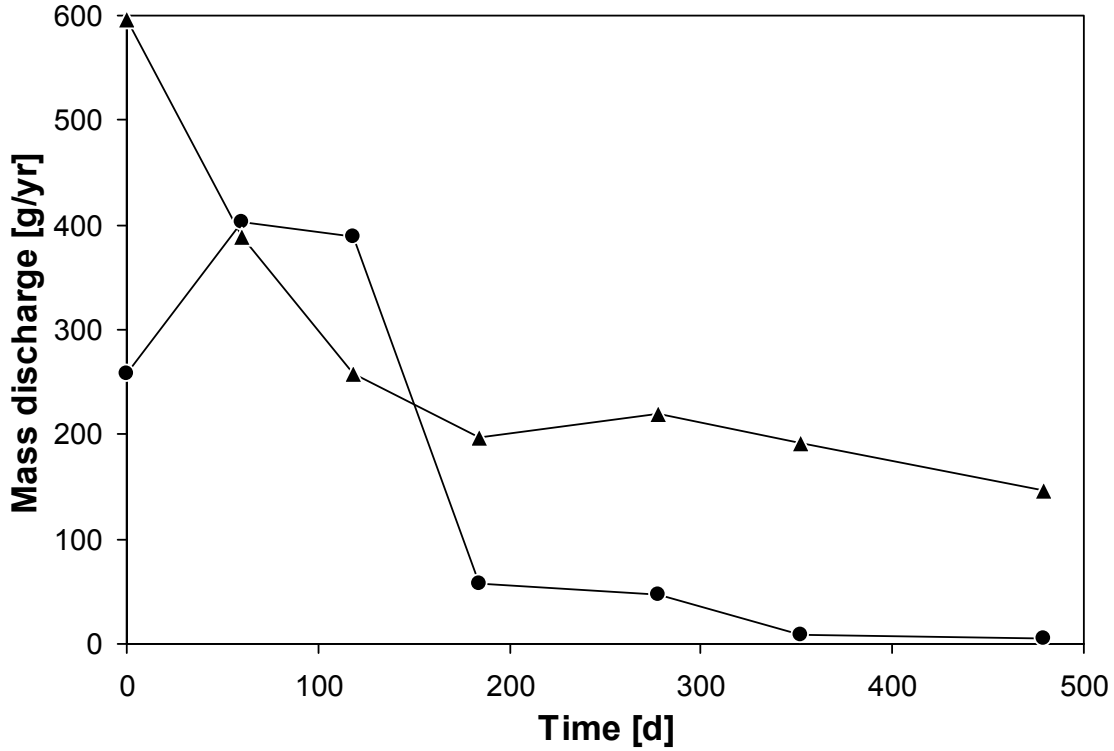

Figure 2.2. Mass discharge of PCE at a control plane (5 m x 13.5 m) 3 m down-gradient of the source zone. Calculated based on conventional monitoring wells with 4 screens (●) and multilevel samplers with 77 screens (▲). (Based on data from Fjordbøge et al., **IV**).

The spatial distribution of contaminant concentrations can vary several orders of magnitude within short distances (e.g., Fjordbøge et al., **IV**; Guilbeault et al., 2005). This may especially be the case at an aging source zone where only narrow lateral DNAPL pools are left (Figure 2.1b). Multilevel samplers will better depict the down-gradient plume when compared to the longer conventional well screens averaging of the concentrations. The higher sampling density of the multilevel samplers improves the certainty of the determined mass discharge and the developed conceptual understanding of solute contaminant transport in the subsurface (e.g., Hatfield et al., 2004; Kübert & Finkel, 2006; Li et al., 2007; Troldborg et al., 2010).

2.3.2 Relationship between mass depletion and mass discharge

The relationship between the mass depletion in the source zone and the mass discharge reduction is of interest when assessing the remedial benefits to the down-gradient receptors. The mass depletion and the mass discharge reduction do not necessarily have a directly proportional relationship (DiFilippo and Brusseau, 2008; McGuire et al., 2006). This makes the prediction of down-gradient mass discharge reduction after source zone remediation challenging.

Several models of varying complexity have been purposed for the determination of the relationship between the source mass depletion and the mass discharge

from the source zone (e.g., Basu et al., 2008; Falta et al., 2005; Jawitz et al., 2005; Parker & Park, 2004; Zhu and Sykes, 2004). One of the simple more commonly used expressions for heterogeneous source zones is the analytical power law model, given by (Falta et al., 2005; Zhu and Sykes, 2004):

$$\frac{M_D(t)}{M_{D0}} = \left(\frac{M(t)}{M_0} \right)^{\Gamma} \qquad \text{(Eq. 2.3)}$$

where M_{D0} is the initial mass discharge [M T^{-1}], $M_D(t)$ is the mass discharge [M T^{-1}] at time t [T], M_0 is the initial source zone mass [M], $M(t)$ is the source zone mass [M] at time t, and Γ is a fitted empirical relationship parameter. The relationship parameter incorporates factors such as source zone architecture, flow field dynamics, and mass transfer processes (DiFilippo & Brusseau, 2008). The relationship parameter (Γ) has been compiled for a number of field applications (~35) utilizing different *in situ* remediation technologies (Brusseau et al., 2007; DiFilippo & Brusseau, 2008; Falta et al., 2005; McGuire et al., 2006). These studies showed that the relationship can generally be represented by values (Γ) close to one (0.5-2), and in most cases (~70 %) below one. Efficient source mass depletion is generally the objective of most aggressive *in situ* remediation technologies. A fast source mass depletion with a somewhat slower corresponding mass discharge reduction is represented by a relationship parameter below one.

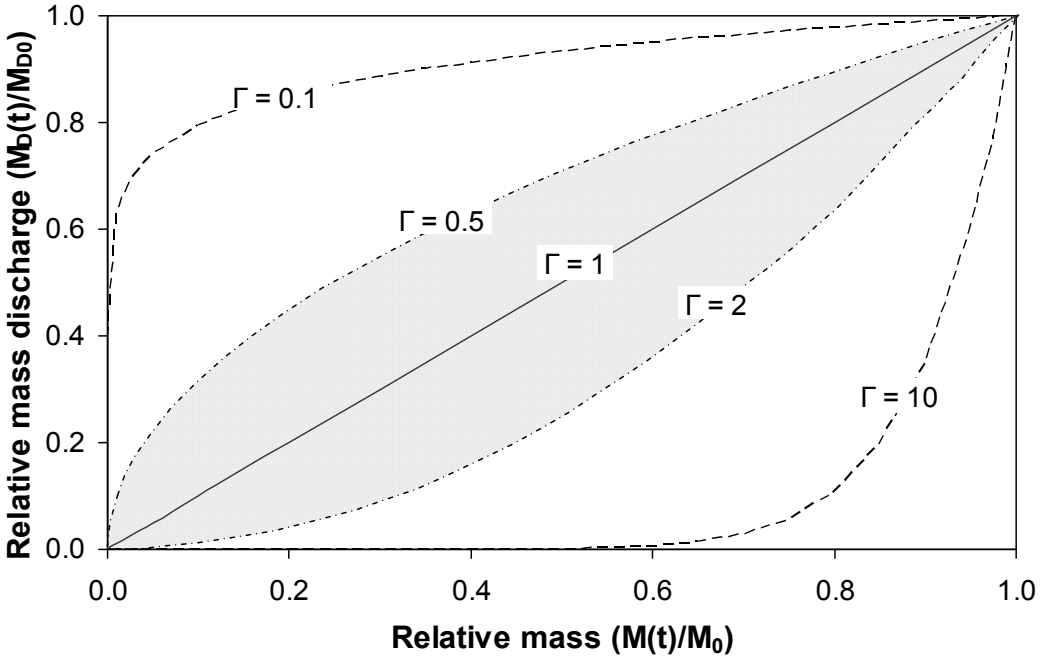

Figure 2.3. Relationship between the source mass and the mass discharge leaving the source when using the power law model (eq. 2.3). For *in situ* remediation technologies the relationship parameter (Γ) has mainly been in the range of 0.5-2 (shaded area).

3 *In situ* remediation technologies

The irregular migration patterns and the slow dissolution of the DNAPL in the subsurface, which were demonstrated in the previous chapter, make site characterization and *in situ* remediation challenging. Based on these factors the prospect of source zone remediation within a reasonable timeframe is limited with the use of classical remediation technologies, such as pump-and-treat. Thus, the development of more aggressive and cost-effective *in situ* remediation technologies suitable for source zone remediation is warranted (Bahr, 1989; Mackay and Cherry, 1989; McGuire et al., 2006, Stroo et al., 2003). The following chapter will give a brief overview of *in situ* remediation technologies; the basic processes common for the ZVI technologies are included.

Several remediation technologies have been under development during the last couple of decades. Generally, two main challenges apply to the development of *in situ* remediation technologies. First, sufficient contact with the source mass must be achieved for efficient depletion to occur. Second, inadvertent spreading of the contaminant to previously unaffected parts of the subsurface due to DNAPL displacement should be avoided (Chown et al., 1997). Hence, the development of *in situ* remediation technologies should focus on both the potential efficiency of the source mass depletion process and the potential risks involved in application of the technology.

The *in situ* remediation technologies can be divided in three main categories based on the primary source mass depletion process. The process can either be chemical (e.g., chemical reduction and chemical oxidation), physical (e.g., thermal treatment and flushing) or biological (e.g., biostimulation and bioaugmentation). Enhanced remedial effects may also be achieved by a combination of complimentary technologies. An overview of some of the more prominent *in situ* remediation technologies is given in Table 3.1.

Table 3.1. Overview of *in situ* remediation technologies for source zones, including an assessment on unit cost for full-scale application, and the number of US Superfund applications.

***In situ* remediation technology**	**Unit cost [$/m^3]**[1]		**Superfund applications**[2]
Chemical technologies:			
Chemical oxidation	150	[26-283]	20
Chemical reduction	-		1
Physical technologies:			
Gas extraction	-		276[3]
Multiphase extraction	-		54
Thermal treatments	168	[42-392]	22
Cosolvent/surfactant flushing	224		19
Biological technologies:	90	[3-294]	65
Biostimulation			
Bioaugmentation			

[1]McDade et al. (2005): average [range]; [2]US EPA (2010); [3]Mainly unsaturated (soil vapor extraction).

3.1 *In situ* chemical remediation technologies

Chemical remediation technologies aim to establish subsurface conditions suitable for abiotic *in situ* transformation of the contaminants to more benign end products through either chemical reduction or chemical oxidation. A risk of inadvertent formation of more hazardous intermediates is involved.

3.1.1 Chemical reduction

Zero valent iron (ZVI) is a chemical reductant, which has primarily been used in permeable reactive barriers for remediation of groundwater plumes. Lately, the research has shifted towards more aggressive *in situ* source zone remediation. The number of applications for source zone remediation is limited compared to the other *in situ* technologies as indicated by Table 3.1.

With a reduction potential of -440 mV, ZVI is a potent chemical reductant for transformation of chlorinated solvents to more benign end products. The basic process for ZVI-mediated reduction of chlorinated solvents has been described in numerous publications (e.g., Gillham & O'Hannesin, 1994; Matheson & Tratnyek, 1994; Scherer et al., 2000). In its simplest form, the process can be given as a reduction of the chlorinated solvent by the release of electrons through ZVI oxidation:

$$\begin{aligned} &Fe^0 \rightarrow Fe^{2+} + 2\ e^- \\ &\underline{RCl + H^+ + 2\ e^- \rightarrow RH + Cl^-} \\ &Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \end{aligned} \qquad \text{(Eq. 3.1)}$$

The specific array of redox reactions at a given site depends on the site specific conditions, including the chemical composition of natural constituents and contaminants in the subsurface. The targeted contaminants are unlikely to be the stoichiometrically most abundant electron acceptors at the site as several other competing electron acceptors (e.g., dissolved oxygen or water) will be present (Gavaskar, 1999; Matheson & Tratnyek, 1994). The reaction with water can be particularly relevant in the saturated subsurface:

$$\begin{aligned} &Fe^0 \rightarrow Fe^{2+} + 2\ e^- \\ &\underline{2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-} \\ &Fe^0 + 2\ H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^- \end{aligned} \qquad \text{(Eq. 3.2)}$$

Several different reaction pathways have been suggested for the transformation of chlorinated solvents (Figure 3.1). The reaction mechanisms include: hydrogenolysis (replacement of one chlorine atom by hydrogen); reductive α- or β-elimination (replacement of two chlorine atoms by hydrogen); and hydrogenation (introduction of hydrogen by the breakage of bonds).

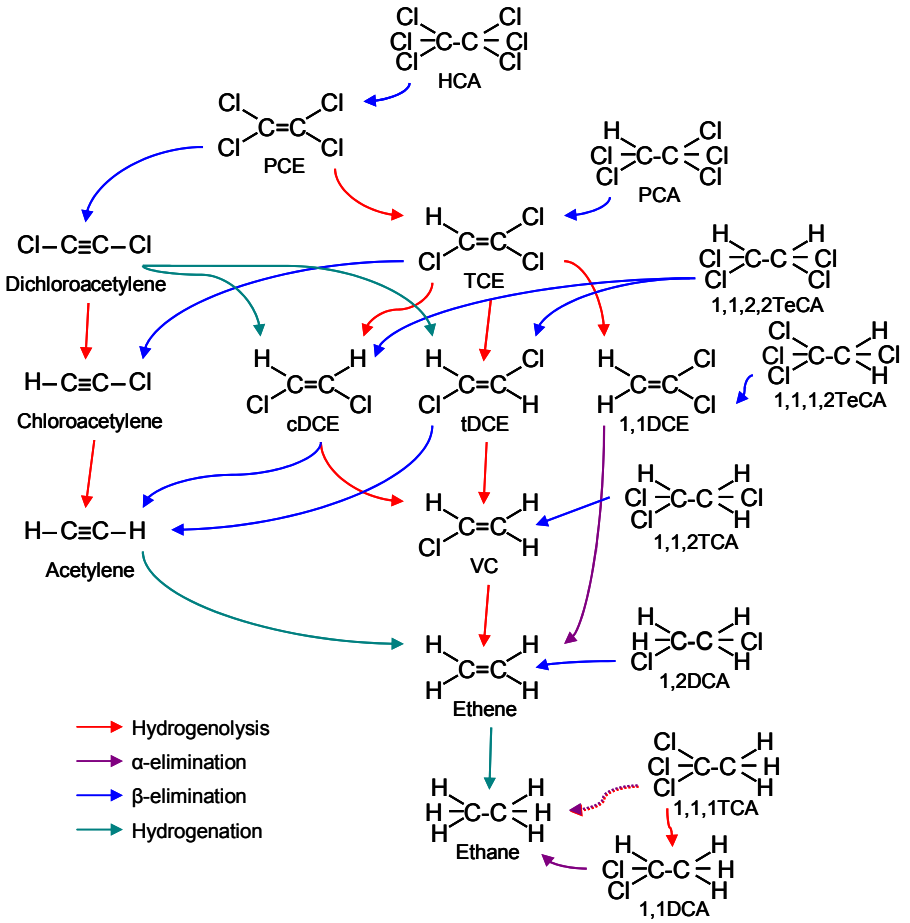

Figure 3.1. Common reaction mechanisms for ZVI-mediated degradation of chlorinated solvents (ethanes and ethenes) (adapted from Arnold et al., 1999).

Studies have shown that the abiotic transformation of chlorinated ethenes primarily occurs through reductive β-elimination to short-lived acetylene compounds, which are further reduced to ethene and ethane (Arnold & Roberts, 2000). Reductive β-elimination also transforms the chlorinated ethanes to chlorinated ethenes in the presence of the necessary α,β-pair of chlorine atoms (Arnolds et al., 1999; Song & Carraway, 2005). The formation of the sequential hydrogenolysis intermediates is limited (Arnold & Roberts, 2000; Arnolds et al., 1999). An extensive production of the sequential hydrogenolysis intermediates has largely been attributed to the co-occurring biotic transformation, which may be stimulated by the uptake of produced H_2 as an electron donor (Fjordbøge et al., **II**; Lampron et al., 2001; Rosenthal et al., 2004). For the chlorinated methanes the preferential pathway is sequential hydrogenolysis (Lien & Zhang, 1999; Matheson & Tratnyek, 1994; Song & Carraway, 2006).

In connection with the development of more aggressive *in situ* remediation technologies, the primary focus has been on the highly reactive nZVI particles (e.g., Li et al., 2006; Wang & Zhang, 1997). The delivery of coarser ZVI and clay to the subsurface by shallow soil mixing is another emerging ZVI

technology which has received limited attention (e.g., Wadley et al., 2005; Fjordbøge et al., **II**, **III**). The development and application of source zone remediation technologies based on ZVI will be the focus of the later chapters.

3.1.2 Chemical oxidation

In situ chemical oxidation utilizes a diverse group of chemical agents for oxidation of the contaminants (e.g., Chen et al., 2001; Dahmani et al., 2006; Gates and Siegrist, 1995; Schnarr et al., 1998; Siegrist et al., 1999; Waldemer et al., 2007; Weeks et al., 2000). *In situ* chemical oxidation is sensitive to subsurface heterogeneities due to delivery by injection (Nyer & Page, 2004), and to the natural oxidant demand in the subsurface (Haselow et al., 2003; Mumford et al., 2005). The challenge of achieving sufficient contact between the contaminant and the injected reagent is demonstrated in a review by Krembs et al. (2010) on more than 200 sites utilizing *in situ* chemical oxidation. The review reports a median reduction of around 55 % for chlorinated volatile organic compounds in the groundwater, while rebound was observed at 62 % of the sites.

3.2 *In situ* physical remediation technologies

Most physical remediation technologies utilize mass transfer processes as a means to source mass removal. The most frequently exploited physical properties are those that allow for enhanced phase transfer into an extractable phase by either increased volatility or solubility (Brooks et al., 2004; Johnson et al., 1993). The use of mass transfer processes and DNAPL displacement involve a risk of inadvertent spreading to previously uncontaminated areas in the subsurface (Brooks et al., 2004; Kaslusky & Udell, 2002; Van Valkenburg & Annable, 2002, Walker et al., 1998). Also, the extracted phase with the contaminants will have to be treated *ex situ* (Brooks et al., 2004; Johnson et al., 1993).

3.2.1 Gas extraction

Gas extraction is one of the early physical *in situ* remediation technologies, which utilizes the partitioning of the volatile chlorinated solvents into a gas phase. The technology can use either: extraction of air injected to the saturated zone via *in situ* air sparging; extraction of soil vapors from the unsaturated zone via soil vapor extraction; or a combined extraction of soil vapors and groundwater via multiphase extraction (Edwards et al., 2002; Gordon, 1998; Johnson et al., 1993). In a heterogeneous saturated subsurface, the introduced buoyant gas phase is generally vulnerable to the formation of gas channels as the preferential flow may bypass parts of contamination (Johnson et al., 1993).

3.2.2 Thermal treatment

Gas extraction can be combined with *in situ* thermal treatment technologies. The vapor pressure of the chlorinated solvents is increased by heating, whereby the mass transfer is faster than at ambient temperatures (Kaslusky & Udell, 2002;

Webb & Phelan, 1997). The different thermal treatment technologies include: steam enhanced extraction with the injection of stream (e.g., Sleep & McClure, 2001; She & Sleep, 1999); electrical resistive heating with the introduction of an electrical current (e.g., Buettner & Daily, 1995; Heron et al., 1998, 2005); and *in situ* thermal desorption with the use of heating elements (e.g., Heron et al., 2009). Thermal treatment has the potential of remediating even low-permeable layers, which has resulted in very high removal efficiencies (>97 %) at several source zones (Heron et al., 2005, 2009; McGuire et al., 2006). The technology is less vulnerable to subsurface heterogeneities than most other technologies, but non-uniform heating can occur (Friis, 2006).

3.2.3 Flushing agents

Cosolvent and surfactant flushing are used to increase the aqueous solubility and the mobility of the hydrophobic DNAPL. The properties of the injected flushing agent(s) promote the mass transfer into an extractable liquid phase (Brandes & Farley, 1993; Brooks et al., 2004; Fountain et al., 1991). For *in situ* flushing to be efficient the entire source zone must be sufficiently accessible to the flushing agent(s); varying removal efficiencies of around 60-99 % have been demonstrated (e.g., Jawitz et al., 2000; Londergan et al., 2001).

3.3 *In situ* biological remediation technologies

Bioremediation aims to enhance the *in situ* biotic transformation of the contaminants to less hazardous compounds. This can be done through biostimulation of the indigenous microorganisms by the addition of nutrients and electron donors, or through bioaugmentation with microorganisms that are more suitable degraders for the specific contaminants (Edstrom et al., 2005; Field & Sierra-Alvarez, 2004; Smatlak & Gossett, 1996). Similar to the chemical remediation technologies there is a risk of the inadvertent formation of more hazardous degradation products.

Natural attenuation is often a slow process whereby enhanced bioremediation can be beneficial. The chlorinated solvents can be degraded anaerobically by different processes depending on the geochemical conditions, and the specific microbial consortium present in the subsurface (Field & Sierra-Alvarez, 2004; Harkness et al., 1999; Heimann et al., 2005; Smatlak & Gossett, 1996). Generally, bioaugmentation shows better results than biostimulation alone as less undesirable degradation intermediates are accumulated (e.g., Edstrom et al., 2005; Harkness et al., 1999; Lendvay et al., 2003; Major et al., 2002; Scheutz et al., 2010). However, biodegradation primarily occurs in the aqueous phase; this limits the potential for rapid source zones remediation (Kaplan et al., 2008; Yang and McCarty, 2000, 2002; Yu & Semprini, 2009). The slow prospect of source zone remediation suggests that bioremediation may have the greatest potential in combination with the more aggressive chemical or physical technologies.

4 The nZVI technology

Nanotechnology is a rapidly developing research area with numerous potential applications in the development of new technologies and the optimization of existing technologies. For the last decade nanotechnology has been utilized in the pursuit of enhanced *in situ* remediation of contaminants in the subsurface. For the ZVI technology the focus has been on the engineering of more reactive and deliverable products at the nanoscale. The properties, environmental fate, remedial efficiency, and possible risks related to the reactive nZVI particles are the focus of the following chapter.

4.1 Characterization and modification

The nZVI technology encompasses a product group with some common overall characteristics; the main common characteristics being the small particle size and the correspondingly large specific surface area (SSA). These characteristics are the driver for the emergence of the nanotechnology. With the decreased particle size the products become deliverable through injection (e.g., Henn and Waddill, 2006; Quinn et al., 2005), while the larger specific surface area allows for a greater reactivity per unit mass. A review by Greiger et al. (**I**) showed that nZVI typically has a specific surface area of around 30 m^2/g and a particle diameter below 200 nm (Table 4.1). This is an increase in the specific surface area, of one to two orders of magnitude, compared to most of the coarser ZVI products (Schrick et al., 2002; Su & Puls, 1999; Wang & Zhang, 1997).

While the overall decreased particle size and the increased specific surface area are common characteristics for the nZVI products, the product group shows a great diversity in their other properties. This diversity is primarily a result of the various applied nZVI synthesis methods, and the vast possibilities for modifying the nZVI surface. Some of the characteristics of the nZVI used for bench-scale studies and field applications have been compiled by Greiger et al. (**I**) and are presented in Table 4.1.

4.1.1 Bimetallic nZVI

The use of bimetallic nZVI (BNP) is a common way to modify nZVI in order to increase the reactivity. The modification is done through the embedment of a second more noble metal on the nZVI surface. The noble metal will act as a catalyst to promote reactivity. Even very small fractions (0.1-1 wt %) of the catalyst metal can significantly increase the nZVI reactivity. A one to two order of magnitude increase in the reactivity has been demonstrated for bimetallic nZVI compared to monometallic nZVI (Lien & Zhang, 1999, 2001; Schrick et al., 2002; Tee et al., 2005; Zhang et al., 1998). The preferred catalyst is palladium (Pd), which has been used in connection with several bench-scale studies and field applications (Table 4.1).

Table 4.1. Characteristics, applications, and remedial efficiencies of nZVI in connection with chlorinated ethenes, ethanes and methanes (revised from Grieger et al., **I**).

Metal	**Size** *[nm]*	**SSA** *[m^2/g]*	**Coating**	**Test type**	**Contaminant**	**Concentration** *[mg/L], *[mg/kg]*	**Removal** *[%]*	**Reference**
Fe^0/Pd	<100	34	None	Batch; water	TCE	20	>99	Wang & Zhang (1997)
Fe^0/Pd	<100	34	None	Batch; water	PCE; TCE	20	>99	Zhang et al. (1998)
Fe^0/Pd	<100	35	None	Batch; water	CT; CF	15	>95	Lien & Zhang (1999)
Fe^0/Pd	<100	35	None	Batch; water	PCE; TCE	20	>95	Lien & Zhang (2001)
Fe^0	<200	31	None	Batch; water	TCE, CF	10	>90	Choe et al. (2001)
Fe^0/Ni	3-30	59	None	Batch; water	TCE	25	>99	Schrick et al. (2002)
Fe^0/Pd	30-100	20-30	PAA	Batch; water	TCE	13	>99	Schrick et al. (2004)
Fe^0/Pd	4-60	55	Starch	Batch; water	TCE	25	>99	He & Zhao (2005)
Fe^0/Pd	<100	34	None	Batch; water	HCA; PCA; TeCA; TCA	20-30	>95	Lien & Zhang (2005)
Fe^0	30-60	23-37	None	Batch; water	TCE	30	52-92	Liu et al. (2005)
Fe^0	80-100	28	None	Batch; water	HCA; PCA; TeCA; TCA	5-25	40-99	Song & Carraway (2005)
Fe^0/Ni	20-40	22-27	None	Batch; water	TCE	10	>90	Tee et al. (2005)
Fe^0	10-80	*N/A*	None	Batch; water	TCE	100	>99	Wu et al. (2005)
Fe^0	~100	10	None	Batch; water	TCE	50	*N/A*	Liu & Lowry (2006)
Fe^0	80-100	28	None	Batch; water	CT; CF	30; 10	85-99	Song & Carraway (2006)
Fe^0/Pd	<18	*N/A*	CMC	Batch; water	TCE	50	>99	He et al. (2007)
Fe^0	<100	23	None	Batch; water	TCE	4-1,100	*N/A*	Liu et al. (2007)
Fe^0	146-212	*N/A*	Triblock	Batch; water	TCE	6	>85	Saleh et al. (2007)
Fe^0	40-45	5-29	None	Batch; water	CT	*N/A*	*N/A*	Sarathy et al. (2008)
Fe^0	*N/A*	23	*N/A*	Column; DNAPL	PCE	>240	30	Taghavy et al. (2010)
Fe^0/Pd	100-200	24	None	Field; plume	TCE	0.80	34-95	Elliott & Zhang (2001)
Fe^0/Pd	<100	*N/A*	*N/A*	Field; plume	TCE	14	>90	Glazier et al. (2003)
Fe^0	*N/A*	*N/A*	*N/A*	Field; plume	TCE; TCA	<2	<90	Varadhi et al. (2005)
BNP	*N/A*	*N/A*	Yes	Field; plume	TCE	3	>95	Hains et al. (2008)
Fe^0/Pd	15-40	*N/A*	CMC	Field; plume	PCE; TCE	0.1	*N/A*	Bennett et al. (2010)
Fe^0/Pd	80-120	29	N/A	Field; plume	VC	5	20-99	Wei et al. (2010)
Fe^0/Pd	*N/A*	*N/A*	Polymer	Field; source	TCE; TCA	224*; 337*	8-92	Henn & Waddill (2006)
Fe^0	*N/A*	*N/A*	*N/A*	Field; source	TCE	2	<96	Chang et al. (2010)
Fe^0	*N/A*	*N/A*	*N/A*	Field; Source	TCE, TCA	86; 8	12-30	Elsner et al. (2010)
Fe^0/Pd	23	*N/A*	CMC	Field; Source	PCE, TCE	12; 24	20-96	He et al. (2010)
Fe^0	100-200	*N/A*	(Emulsion)	Field; DNAPL	TCE	6,100*	26-99	Quinn et al. (2005)

4.1.2 Surface coatings

The addition of surface coatings is an increasingly common way to modify the mobility and the stability of nZVI; these properties are important for the deliverability to the contaminated subsurface. Uncoated nZVI is prone to rapid aggregation, which leads to a loss of environmental mobility through colloidal filtration mechanisms, and subsequent clogging of the porous media. Hence, the primary objective of the surface coatings is to limit aggregation and sustain discrete particles (He and Zhao, 2005; Schrick et al., 2004).

The surface coatings rely on electrostatic repulsion and/or steric hindrance to prevent the attraction between the nanoparticles and the attachment to the porous media (He et al., 2007; Saleh et al., 2007). Polymers, polyelectrolytes, and surfactants are the primary surface coatings (Table 4.1), which include starch (He and Zhao, 2005), poly(acrylic acid) (PAA) (Schrick et al., 2004), proprietary polymers (Henn & Waddill, 2006), carboxymethyl cellulose (CMC) (Bennett et al., 2010; He et al., 2007, 2010), and triblock copolymers (Saleh et al., 2007).

The effect of the surface coatings on the reactivity of nZVI is less straightforward than the effect on the mobility and the stability. The prevention of nZVI aggregation can promote the reactivity as the aggregation into larger clusters decreases the reactive surface area. This effect can be counteracted by the fact that the bulky surface coatings block some of the reactive site on the nZVI surface (Saleh et al., 2007). Hence, there may be some trade-off between deliverability and reactivity.

4.1.3 Targeting of the DNAPL-water interface

The nZVI technology is vulnerable to the same limitations as other injection based technologies (e.g., *in situ* chemical oxidation or *in situ* flushing). The limitations related to the delivery method become even more pronounced with the injection of reactive particles instead of liquid agents (Nyer & Page, 2004). As previously described, one of the main challenges is the limited contact between the injected reagent and the contaminants. DNAPL-water interface targeting is one of the latest technological advances to overcome the contact limitations. The development of a surface coating that promotes DNAPL-water interface targeting has the potential of decreasing the dependency on DNAPL dissolution. This can promote the direct depletion of the contaminated mass in the source zone.

The ability of coated nanoparticles to self-assemble at liquid-liquid interfaces has been shown by Lin et al. (2003). Consequently, researchers have sought to apply this to the nZVI technology to achieve DNAPL-water interface targeting. The first step has been the engineering of a triblock copolymer surface coating for nZVI. The triblock copolymer coating is described to function via: an adsorbing block anchoring the coating to the nZVI; an anionic hydrophilic block providing

the repulsion needed for mobility; and a hydrophobic block providing a preferential affinity for the DNAPL. These properties should enable the nZVI to migrate through the subsurface until a DNAPL-water interface is encountered (Saleh et al., 2005). The affinity of the triblock copolymer coated nZVI for the NAPL-water interface has been tested in bench-scale studies. Saleh et al. (2005) showed the ability to form oil-in-water (o/w) emulsions stabilized with the coated nZVI particles (0.3 wt % copolymer), while Saleh et al. (2007) demonstrated the ability for retention in columns with dodecane coated sand grains (NAPL-water interface). However, the later study showed that less than 10 % of the nZVI was retained in the column. Hence, the advanced surface coating shows a potential for a technological improvement with targeting of the contaminants (DNAPL) in the source zone, but further optimization is warranted prior to field application.

4.2 Subsurface fate of nZVI

Two of the most important factors for the fate of nZVI in the subsurface are the persistence of nZVI as a reactive nanoparticle and the spreading of nZVI. The research related to the subsurface fate of nZVI is mainly based on bench-scale studies under ideal conditions. Reports on field data are gradually increasing, although still largely based on observed secondary effects (e.g., oxidation-reduction potential, pH, dissolved oxygen and color). For the field applications the diversity of the various nZVI products will surely affect the fate of the particles in the subsurface; however, nZVI products are generally not thoroughly characterized for the field application (Table 4.1). This all adds to the uncertainty of the assessment of the subsurface fate of nZVI (Greiger et al., **I**).

4.2.1 Persistency

The persistency of nZVI is strongly related to the reactivity of nZVI. In the subsurface, nZVI will undergo oxidation as it ages. During the aging process nZVI is primarily transformed to magnetite (Fe_3O_4) and/or maghemite (Fe_2O_3, γ-Fe_2O_3) (Nurmi et al., 2005; Reinsch et al., 2010). The nZVI remains reactive during the aging process until the reactive ZVI (Fe^0) particle core has been depleted (Liu & Lowry, 2006). The rate of the aging process depends on the reactivity of nZVI; the faster the particle reacts with the various electron acceptors in the subsurface, the faster it oxidizes. The reactive life time of nZVI will therefore depend on the characteristics of the particles, and the reaction with both the contaminants and other more abundant electron acceptors (e.g., water, eq. 3.2). Early estimates of the reactive life time of nZVI were on the order of one year (e.g., Schrick et al., 2002). Later studies have shown that a reactive life time on the order of days to weeks may be more realistic, depending on the structure and size of the nZVI product (He et al., 2007; Liu et al., 2005). Based on these observations, nZVI is not expected to persist as highly reactive particles for an extended time period following the release to the subsurface.

4.2.2 Mobility

The spreading of nZVI in the subsurface depends on the applied surface modifications for enhanced mobility and the applied methods of injection. In general, the nZVI slurries used for source zone injections contain high particle concentrations. A typical concentration range of 1-10 g/L has been determined (Bennett et al., 2010; Elliott and Zhang, 2001; Elsner et al., 2010; Glazier et al., 2003; Greiger et al, **I**; He et al., 2010; Henn and Waddill, 2006).

For the uncoated nZVI the migration in the subsurface will be significantly limited by the formation of aggregates. The combination of aggregation and high particle density in the injected slurry promotes the colloidal filtration mechanism, and subsequent clogging of the porous media at the injection point. Consequently, the uncoated nZVI is only expected to migrate a few centimeters beyond the injection point (Saleh et al., 2007; Schrick et al., 2004; Tratnyek and Johnson, 2006). Unless an accurate site characterization has been performed, this limits the potential of achieving contact with the contaminants.

The emergence of the various mobility promoting surface coatings for nZVI has increased the potential radius of impact from the injection point; the modified repulsive characteristics enable considerably longer migration distances before nZVI is attached to the porous media. It has been suggested that the migration distance can be increased to tens or possibly hundreds of meters at favorable flow and geochemical conditions (He et al., 2009; Saleh et al., 2007, 2008; Schrick et al., 2004; Tratnyek and Johnson, 2006). However, field applications generally show more moderate migration distances of around 3-6 meters (Elsner et al., 2010; Henn & Waddill, 2006; Wei et al., 2010). With the high particle concentrations used for field applications, even the coated nZVI may agglomerate and deposit close to the injection point (Phenrat et al., 2009a, 2010).

The longevity of the enhanced mobility will depend on the desorption and the biodegradation of the applied coatings. To date, the longevity of the coatings has received little attention (Greiger et al., **I**). However, slow desorption of a polyelectrolyte coating has been demonstrated in a bench-scale study; the coating kept nZVI mobile for at least eight months (Kim et al., 2009). Also, carboxymethyl cellulose applied as a surface coating may act as a carbon source for biodegradation (He et al., 2010). The processes affecting the longevity of the surface coating generally appear to be slow when compared to the expected reactive life time of the nZVI. Hence, the persistency of the nZVI particle will be more important for the subsurface fate than the persistency of the coating.

4.3 Site remediation

Remediation of chlorinated solvents by the nZVI technology is claimed to have several benefits when compared to the technologies with coarser ZVI products. These benefits include superior degradation rates (Lien & Zhang, 2001; Schrick et al., 2002; Wang & Zhang, 1997; Zhang et al., 1998) and limited production of undesirable degradation intermediates (Lien & Zhang, 2001, 2005; Liu et al., 2005). The assertion is based on bench-scale studies, which are the primary data source for nZVI efficiency. These studies generally report on idealized aqueous systems with contaminant concentrations below 30 mg/L (Table 4.1). Under these conditions, high removal efficiencies (90-99 %) can generally be achieved, since the efficiency primarily depends on the dosage of nZVI and the duration of the study. The capability of nZVI to degrade chlorinated solvents is unambiguous; however, one of the reviewed bench-scale studies indicates that source zone remediation will be challenging as the removal efficiency is reduced considerably in the presence of DNAPL (Taghavy et al., 2010). The potential of source zone remediation with nZVI can not be sufficiently assessed based on aqueous bench-scale studies. Upscaling to field application is required for an improved assessment of the nZVI technology.

4.3.1 Field applications

The number of field applications with the nZVI technology is continuously increasing around the world. To date, the nZVI technology appears to have been applied at around 40 contaminated sites, none of these in Denmark (PEN, 2011). The nZVI technology has primarily been applied in the United States; in 2008 the US EPA had 26 sites on their list of sites using or testing nanoparticles for remediation (US EPA, 2008). Only a few of the field applications have been reported on in the literature.

The remedial efficiencies vary considerably for the field applications. While most bench-scale studies showed more than 90 % removal, the field applications show a broader range of removal efficiencies for contaminated groundwater. The removal efficiencies in the field range from practically no degradation to almost complete remediation (Table 4.1). These observations apply to both the early applications with uncoated nZVI and the later applications with coated nZVI. The variable removal efficiencies for application of nZVI are comparable to the other previously described injection based technologies, such as *in situ* chemical oxidation and *in situ* flushing (chapter 3).

The collected data show that most of the field applications (~80 %) have targeted contaminated groundwater with relatively low contaminant concentrations (Bennett et al., 2010; Elliott & Zhang, 2001; Glazier et al., 2003; Hains et al., 2008; PEN, 2011; US EPA, 2008; Wei et al., 2010). The nZVI technology is able to achieve a relatively high removal efficiency in the contaminated plume close

to the point of injection. Hence, the remediation of contaminated groundwater plumes with the nZVI technology can be efficient with a dense injection grid.

Source zone remediation has proved more challenging; the few reported source zone applications show a considerable variation in the remedial efficiencies (Table 4.1). The poorer remedial efficiencies are seen as the result of heterogeneity limitations related to the delivery by injection and the detection of the DNAPL in the subsurface. DNAPL was not detected at any of the treated source zones; however, elevated soil and groundwater concentrations indicated the presence of DNAPL in the source zones (Chang et al., 2010; Elsner et al., 2010; He et al., 2010; Henn & Waddill, 2006). Consequently, groundwater concentrations have rebounded at these sites.

In connection with the limited contact between the ZVI and the contaminants, the high reactivity of nZVI is not necessarily a benefit for source zone remediation. The rapid reaction with competing electron acceptors can reduce the reactive life time of nZVI, and exhaust the reactive potential of nZVI before the contaminants are completely depleted (He et al., 2010; Fjordbøge & Kjeldsen, 2008; Greiger et al., **I**; Liu et al., 2007). Without sufficient contact between the nZVI and the contaminant, several reinjections are required for source zone remediation.

Currently, the injection of emulsified nZVI is the most efficient application of the nZVI technology for source zone remediation. Although emulsified nZVI is only used in a minor fraction (~10 %) of the total field applications, it has been utilized at almost half of the sites with high contaminant concentrations (>30 mg/L) (PEN, 2011). The technology encapsulates the nZVI into the droplets of a surfactant-stabilized biodegradable o/w emulsion. The o/w emulsion protects the ZVI from competing electron acceptors in the form of inorganic or polar groundwater constituents. The o/w emulsion allows contact with hydrophobic organic constituents with an affinity for the oil (Berge & Ramsburg, 2009; Quinn et al., 2005). Quinn et al. (2005) demonstrated that emulsified nZVI reduced groundwater concentrations (57-99 %) and soil concentrations (26-99 %) in the source zone without observation of rebound. Under certain hydraulic conditions the injection of an o/w emulsion may mobilize DNAPL in the source zone like a flushing agent; caution should be taken to minimize the risk of DNAPL displacement (Berge & Ramsburg, 2009). The technology utilizes the synergy between the ZVI technologies and bioremediation by combining abiotic ZVI degradation with biostimulation (i.e., biodegradable oil). Hence, the formation of the sequential hydrogenolysis intermediates has been observed (Quinn et al., 2005). The formation of the sequential hydrogenolysis intermediates is not limited to the emulsified nZVI technology. Although bench-scale studies have shown little or no production of these intermediates for the non-emulsified nZVI, the intermediates are still observed under field conditions (He et al., 2010; Henn & Waddill, 2006).

4.4 Risks related to nZVI application

Apart from the general risks related to injection based remediation technologies, the field application of the nZVI technology includes additional more uncertain risks; these risks are related to the introduction of nanoparticles to the environment. The emerging nanotechnologies involve the concern of possible adverse effects upon contact with the nanoparticles. A precautionary approach towards nanoparticles has been suggested based on early warning and late lessons learned from other proclaimed beneficial technologies (e.g., Hansen et al., 2008; Moore, 2006).

In connection with nZVI the potential risks are to the receptors in the source zone, and as the mobility of the particles is enhanced also to the down-gradient receptors. Several factors affect the assessment of the risk of introducing nZVI to the subsurface. These factors have been a focus area in a review on potential benefits and risks of nZVI done by Greiger et al. (**I**). The factors include the persistency, mobility, toxicity, and bioaccumulation of nZVI in the subsurface, which can be compared to the risk reduction from degradation of the contaminants. The previous assessment of the fate of nZVI in the subsurface in terms of persistency and mobility (chapter 4.2) showed that the high reactivity of nZVI limits the reactive life time (days to weeks) in the subsurface, while even surface modified particles are expected to have limited mobility (a few meters). Unfortunately, the most desirable nZVI characteristics for site remediation are also the characteristics that hold the greatest risk potential. The future optimization of the reactivity and mobility of nZVI for better remedial performance may consequently increase the potential risk.

The adverse effects of nZVI are dominated by a high degree of ignorance (Greiger et al., **I**). The potential for bioaccumulation is generally unknown, and the ecotoxicity has only been investigated in a few studies (Auffan et al., 2008; Cullen et al., 2011; Lee et al., 2008; Li et al., 2009, 2010; Phenrat et el., 2009b; Xiu et al., 2010). The use of traditional toxicity tests, developed for chemical compounds, for determination of nanotoxicity adds to the uncertainty of the assessment (Hartmann et al., 2010), as does the ability of certain nanoparticles to act as contaminant carriers (Baun et al., 2008).

With limited data on basically all the key metrics in environmental risk assessment (i.e. persistency, bioaccumulation, and toxicity), the assessment of the potential environmental risks of nZVI will evidently be uncertain at the present time (Greiger et al., **I**). There are no data showing that nZVI poses a severe apparent risk to the environment. However, elaborate monitoring of the mobility, persistency, and long-term ecotoxicological effects of nZVI following field application is called for to reduce the assessment uncertainties.

5 The ZVI-Clay soil mixing technology

Subsurface heterogeneities generally limit efficient source zone remediation. Hence, the development of alternative methods for more efficient ZVI delivery is of interest in the pursuit of enhanced source zone remediation. The ZVI-Clay soil mixing technology uses such an alternative method to overcome the limitations associated with subsurface heterogeneities. Although the ZVI-Clay soil mixing technology holds great promise for efficient remediation of source zones with free phase DNAPL, the technology has received limited attention. During the last decade only nine full-scale field application of ZVI-Clay soil mixing have been conducted (Fjordbøge et al., **II**). The following chapter will focus on the remedial efficiency, the soil mixing process, and the limitations of the emerging ZVI-Clay soil mixing technology.

5.1 The concepts behind ZVI-Clay soil mixing

The ZVI-clay soil mixing technology combines the following three concepts (Fjordbøge et al., **II**):

- Source mass depletion by addition of a reactive agent (ZVI).
- Containment by addition of a stabilizing agent (clay) in the drilling fluid.
- Subsurface delivery and homogenization through soil mixing of the added agents, the contaminated media, and the contaminants (incl. DNAPL).

The conceptual model of ZVI-Clay soil mixing is illustrated in Figure 5.1. The soil mixing ideally disperses any DNAPL and low-permeable geological layers in the source zone. The addition of ZVI and clay creates a reactive low-permeable mixture that is bypassed by the groundwater flow.

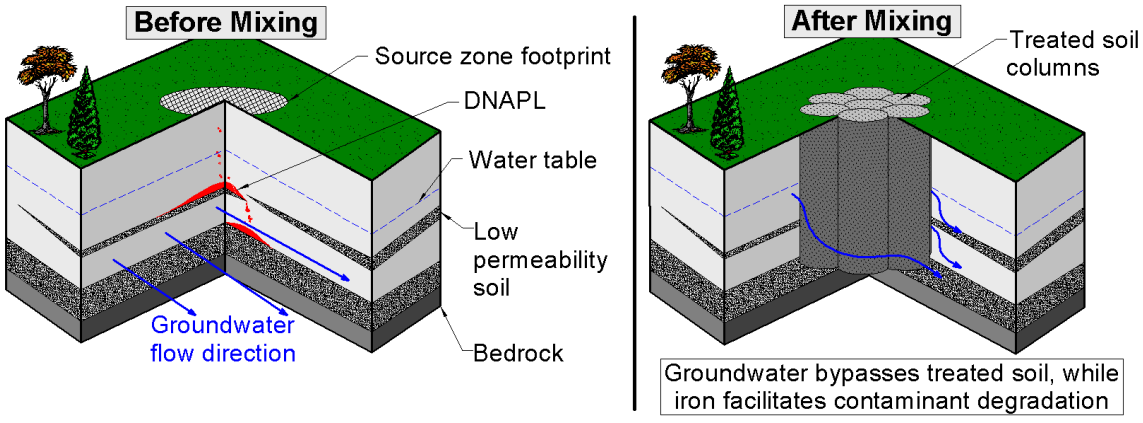

Figure 5.1. Conceptual model of ZVI-Clay soil mixing: (left) the heterogeneous subsurface architecture before soil mixing, and (right) the homogenized low-permeable subsurface after soil mixing with bypassing groundwater (CSU, 2007; with permission).

The concepts behind the ZVI-Clay soil mixing technology have been used individually in various technological disciplines. As already described in this thesis, ZVI is a well-known reductant for chlorinated solvents. Clay is used in other connections to confine contaminants and prevent migration through the subsurface; an example is the common use of bentonite liners, with low hydraulic conductivity, in connection with waste management at landfills (Allan, 2001). Shallow soil mixing has been used for soil stabilization with cement, lime and/or fly ash (Larsson, 2005; Liu et al., 2011). The combination of these interdisciplinary areas presents new possibilities and challenges.

5.2 Source zone remediation

The ZVI-Clay soil mixing technology has demonstrated efficient reduction of chlorinated solvents (methanes, ethanes and ethenes) in bench-scale studies and field applications (e.g., Fjordbøge et al., **II**, **III**, Wadley et al., 2005). Most of the field applications have included a limited number of post-mixing sampling campaigns, which makes the determination of reactions rates in the field uncertain. However, the bench-scale studies have demonstrated average half-lives of a few days for the chlorinated methanes and a few weeks for the chlorinated ethanes and ethenes (Fjordbøge et al., **II**). The faster degradation of the chlorinated methanes was also observed for the field applications (Fjordbøge et al., **II**).

The use of soil mixing as the delivery method potentially improves the contact between the reactive ZVI and the source zone contaminants. Consequently, high removal efficiencies (>80 %) have been reported for all the full-scale field applications at contaminated source zones (Fjordbøge et al., **II**). The source mass depletion is generally accompanied by reduced groundwater concentrations. The reduction of the source mass and the groundwater concentrations are summarized in Table 5.1.

Table 5.1. Overview of ZVI-Clay soil mixing field applications, including: initial contamination and removal efficiencies after around one year; typically amounts of ZVI and clay; and unit cost (mobilization, materials, mixing, demobilization) for the remediation (modified from Fjordbøge et al., **II**).

Site #	Compound	Concentration *[mg/kg]*	Volume *[m^3]*	Iron; Clay *[% dry]*	Avg. removal *[%] Soil; water*		Cost *[$/$m^3$]*
A	TCE	25-50	200	*N/A*	~90;	*N/A*	*N/A*
B[a]	CT	4,000	3,000	2-6; 6	>99;	*N/A*	105
C[b]	PCE	430-2,700	5,400	2; 1	82;	96	95
D	TCE	<27[1]	1,700	1.5; 1	*N/A*;	~85	*N/A*
E	PCE, TCE	2	900	2; 1	>98;	>98;	230
F	TCE	*N/A*	5,400	2; 1	*N/A;*	*N/A;*	235
G[c]	CT, CF, TCA	8,000	900	~2; 4	>99;	~90	235
H[d]	TCE, TCA	116	23,000	2; 3	96;	89	60
I[e]	PCE	22-12,000	200	3; 1	>99;	76	420

[1]mg/L; [a]Shackelford et al. (2005); [b]Bozzini et al. (2006); [c]Ovbey et al. (2010); [d]Olson et al. (submitted); [e]Fjordbøge et al. (**III**; **IV**).

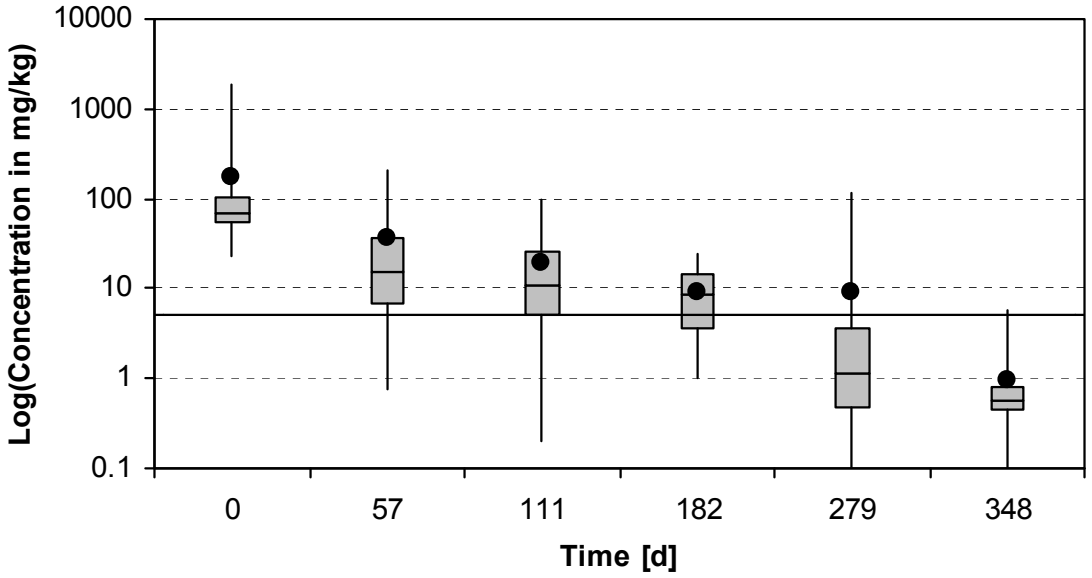

Figure 5.2. Box plot of the decline in PCE concentrations (logarithmic) over time following ZVI-Clay soil mixing with 3 % ZVI and 1 % bentonite at a field site in Skuldelev, Denmark (○: mean; box: interquartile range; whiskers: extrema; soil quality criteria: full line). Pre-mixing concentrations were in the range 22-12000 mg/kg (based on Fjordbøge et al., **III**).

For most of the ZVI-Clay soil mixing field applications DNAPL was detected during site characterization, while elevated concentrations at the other sites indicate that DNAPL was present (Bozzini et al., 2006; Fjordbøge et al., **II**, **III**; Wadley et al., 2005). Fjordbøge et al. (**III**) showed an overall reduction in soil concentrations of more than two orders of magnitude within a year (Figure 5.2). This reduction seems achievable at most sites with chlorinated ethenes and ethanes, while the chlorinated methanes in general were reduced more than four orders of magnitude within a similar time period (Fjordbøge et al., **II**; Shackelford et al., 2005).

At one site, slower source mass depletion was observed in the part of the source zone that contained free phase DNAPL, when compared to the remaining part of the source zone (Bozzini et al., 2006). This does not appear to be a general problem for the ZVI-Clay soil mixing technology, but rather a site specific problem. The detailed study by Fjordbøge et al. (**III**) showed rapid source mass depletion in the entire source zone, also where free phase DNAPL was detected before ZVI-Clay soil mixing.

5.3 Soil mixing and homogenization

Soil mixing without the stabilizing clay agent has previously been used in combination with vapor extraction for improved site remediation. Although significant removal was achieved (>85 %) a tracer test showed that the soil homogenization process was restricted to a limited inward and upward translocation of the soil (Siegrist et al., 1995). It was suggested that soil mixing

could be improved by modifications to the auger, which could also allow the delivery technology to be used in combination with reactive agents (e.g., ZVI). The ZVI-Clay technology encompasses the use of a clay slurry (drilling fluid) to improve the soil mixing process, and the desired outcomes in terms of homogenization and reduced hydraulic conductivity.

5.3.1 Vertical homogenization

The vertical homogenization process can be assessed based on the ability to disperse different geological layers and to deliver a uniform concentration of contaminants and ZVI with depth. Wadley et al. (2005) added ZVI to the clay slurry and found that well-mixed conditions were achieved for ZVI after three auger strokes, but contaminant concentrations still increased with depth. Hence, a complete homogenization was not achieved, but it was suggested that better homogenization could be achieved with larger scale commercial augers (Figure 5.3). Field implementation with the use of commercial augers has since been performed (Bozzini et al., 2006; Fjordbøge et al., **II**, **III**; Shackelford et al., 2005). Other soil mixing tools have also been successfully employed (Fjordbøge et al., **II**; Ovbey et al., 2010), but the soil mixing is less uniform with these tools.

ZVI-Clay soil mixing has successfully been applied to different geological settings. These include: relatively homogeneous sandy aquifers; heterogeneous aquifers with embedded low-permeable layers; and overconsolidated silty clays (Fjordbøge et al., **II**). Visual inspections at one site have shown the dispersion of an organic rich layer (peat) into the full targeted depth of a sandy aquifer. The dispersion was achieved by six auger strokes (Fjordbøge et al., **III**).

Figure 5.3. Equipment typically used for shallow soil mixing with ZVI and clay; (left) a crane used for the soil mixing, and (right) the auger used for soil mixing. (From the site reported on in Fjordbøge et al., **III**, **IV**).

The vertical distribution of iron depends on the approach used for addition of ZVI. With a few auger strokes the simultaneous addition of both ZVI and clay through the drilling fluid provides the most uniform dosing and distribution of iron. At one site this approach resulted in a relatively uniform distribution of ZVI with depth; the content of ZVI only declined 0.1 % per meter (Fjordbøge et al., **II**). A larger variation with depth was found when a top-down addition of ZVI to terrain was applied (Figure 5.4). The average iron content decreased with 0.5 % per meter, while the average oxidation-reduction potential increased 35 mV per meter (Fjordbøge et al., **III**). When applying a top-down addition of ZVI, the homogenization could benefit from additional auger strokes during the soil mixing process.

The variability in iron content still resulted in similar end points for source mass depletion at all of the sampling locations (Fjordbøge et al., **III**). The primary reason for this is the stoichiometrical surplus of ZVI generally added in the field applications. On average, the field application reported by Fjordbøge et al. (**III**) fulfilled the goal for the applied iron content. However, ZVI-Clay soil mixing should preferably target minimum iron contents rather than average iron contents (Fjordbøge et al., **II**). This is worth keeping in mind when using the top-down addition of ZVI.

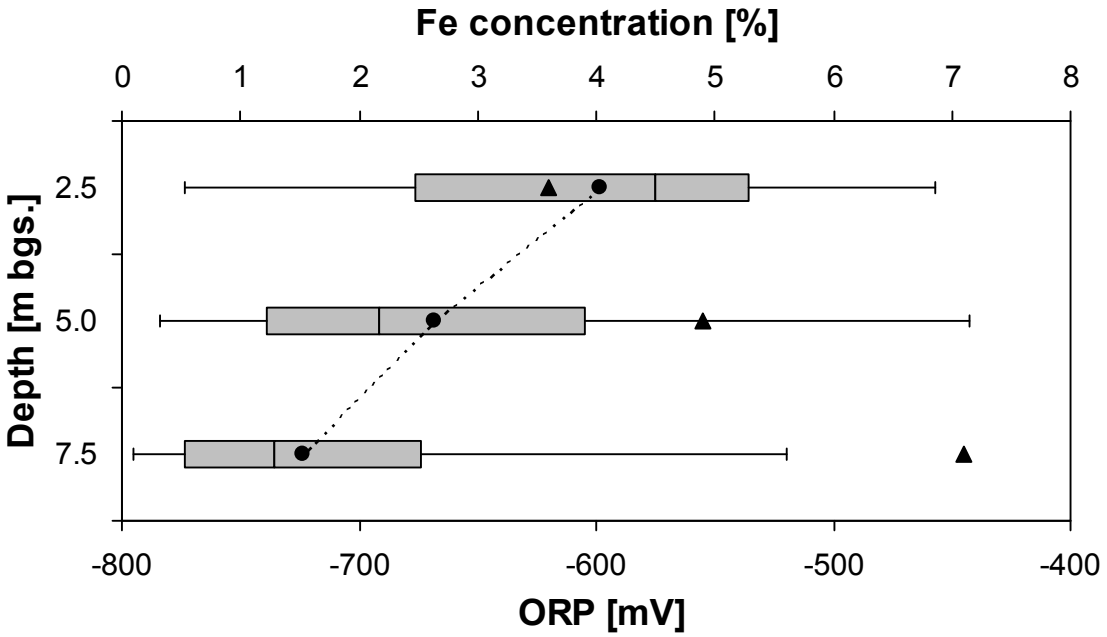

Figure 5.4. Box plot of the distribution of total iron (background corrected) with depth as a measure of soil homogenization following top-down addition of ZVI (●: mean; box: interquartile range; whiskers: 5th and 95th percentile), and the oxidation-reduction potential with depth (▲) (modified from Fjordbøge et al., **III**).

A few percent of ZVI can be suspended in the clay slurry without any significant alterations to the slurry viscosity (Fjordbøge et al., **II**); however, the relatively high density of ZVI will increase the density of the drilling fluid. The increased density will not only increase the strain on the soil mixing equipment, but also increase the risk of fracturing the surrounding formation. The greater hydrostatic pressure in the column compared to the surroundings will increase the risk of driving the drilling fluid into the formation (Borchardt, 2010). The risk of formation fracturing has not been examined in connection with the ZVI-Clay soil mixing technology.

Limited investigations have been conducted on the vertical distribution of contaminants following soil mixing. Generally, the comparison of the pre-mixing concentrations at site characterization with the post-mixing concentrations showed less variability after soil mixing (Bozzini et al., 2006; Fjordbøge et al., **III**; Wadley et al., 2005). There was still a tendency for the highest concentrations to be at the same approximate depths before and after soil mixing (Fjordbøge et al., **III**; Wadley et al., 2005). Fjordbøge et al. (**III**) found that the post-mixing concentrations varied within the same order of magnitude in 80 % of the samples from the same vertical profiles. Before the soil mixing the norm was a variation of more than two orders of magnitude, after the soil mixing less than 2 % of the samples from the same vertical profile varied this much.

The experiences from the field showed that the ZVI-Clay soil mixing technology has certain limitations with regard to vertical homogenization. However, post-mixing conditions were significantly more uniform than pre-mixing conditions.

5.3.2 Horizontal homogenization

Limited horizontal homogenization has been demonstrated following ZVI-Clay soil mixing (Figure 5.5). Horizontal mixing may occur between the neighboring soil columns, especially since ZVI-Clay soil mixing normally is performed with 10 % overlap between the soil columns. The overlap is included to avoid the formation of subzones without any addition of ZVI.

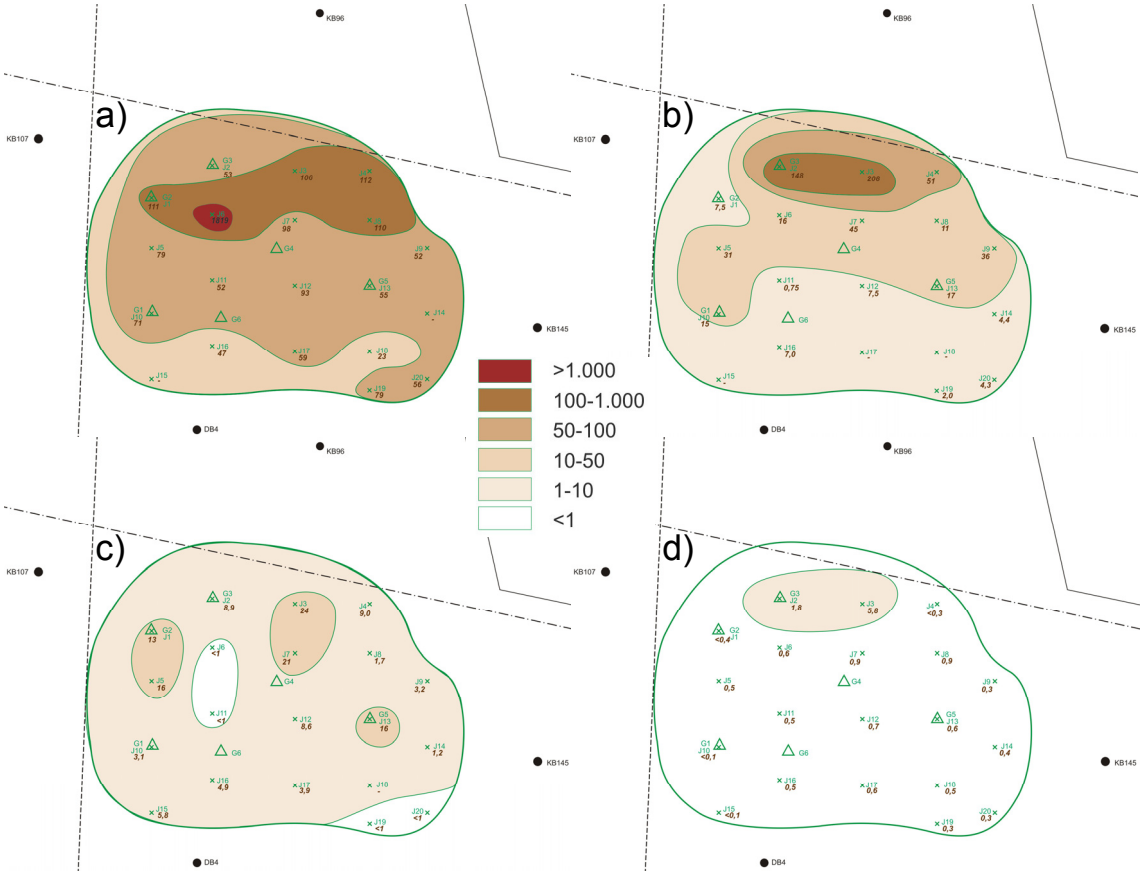

Figure 5.5. Horizontal distribution of the contaminant (PCE) in mg/kg a) 0; b) 2; c) 6; and d) 12 months following ZVI-Clay soil mixing. The dotted line through the area is the approximate location of the old sewer from where the contamination originates (from Fjordbøge et al., **III**).

The assessment of the horizontal homogenization is based on the observation that the highest concentrations of the contaminants occur in the same locations at both the pre- and post-mixing sampling campaigns (Fjordbøge et al., **III**).

The lack of horizontal homogenization is not a limitation on the ZVI-Clay soil mixing technology. In fact, the preservation of a heavily contaminated center of the source zone and a less contaminated perimeter allows for a possible division into several contaminated subzones. The ZVI addition goals can then be adjusted as the soil concentrations decreases with increasing distance to the central part of the source zone. This may especially be beneficial at larger source zone in order to reduce material cost.

5.3.3 Importance of clay addition

The addition of clay to the drilling fluid has multiple functions. During the soil mixing process, the functions of the clay are to facilitate a homogeneous soil mixing process and to lubricate the soil mixing equipment. After the soil mixing process, the function of the clay is to contain the contaminants by reducing the

hydraulic conductivity. The selection of the right type of clay is thereby of importance for several processes both during and after soil mixing.

Clays belong to a very diverse material group (Grim, 1962). The material group can be divided into two main subgroups based on the structural layering of the clay, namely the swelling and the non-swelling clays. The two types of clay have different properties. Bench-scale studies with a representative for each subgroup of clay have been carried out in connection with the ZVI-Clay soil mixing technology to find the superior type of clay (Fjordbøge et al., **II**). The studies included bentonite (swelling clay) and kaolin (non-swelling clay).

Drilling fluid properties depend on the viscosity and the density of the fluid. For ZVI-Clay soil mixing, appropriate drilling fluid values are considered to be a viscosity of 38-45 Marsh funnel (MF) seconds and a density of 1.04-1.08 g/cm^3 (Fjordbøge et al., **III**). To achieve a viscosity of around 45 MF seconds the clay demand of the drilling fluid is more than three times higher for kaolin than for bentonite, resulting in relatively high densities for kaolin slurries (Fjordbøge et al., **II**). As previously described, too high densities are undesirable due to risks of formation fracturing. Minimizing the material demand is desirable, whereby bentonite has the superior characteristics for a ZVI-Clay soil mixing drilling fluid.

The reduced hydraulic conductivity of the source area is important as it affects: the contaminant containment, the reactive residence period, and the inflow of competing electron acceptors to the source zone. Bench-scale studies on the reduction of hydraulic conductivity from soil mixing showed that the main homogenization originated from the soil mixing process itself (around two to three orders of magnitude). The addition of bentonite could further decrease the hydraulic conductivity (around one order of magnitude), while the addition of kaolin did not have any significant effect on the hydraulic conductivity (Fjordbøge et al., **II**). Limited field data exist on the pre- and post-mixing hydraulic conductivities. Bozzini et al. (2006) carried out post-mixing slug tests in wells inside and outside of the source area; a difference of one to two orders of magnitude was determined. Another field application showed a decrease in the permeability of more than four orders of magnitude (Fjordbøge et al., **II**). The exact reduction of the hydraulic conductivity will likely depend on the specific characteristics related to the site and the soil mixing procedure. However, even a minor reduction of the hydraulic conductivity in the source zone will significantly change the flow pattern of the area. Modeling has shown that the down-gradient effects on mass discharge with a reduction of the hydraulic conductivity of one to two orders of magnitude are similar to the effects with a reduction of 3-6 orders of magnitude (Jørgensen, 2008).

Finally, the ability to form Pickering emulsions was tested for the two types of clay. Pickering emulsions are emulsions that are stabilized by a colloidal solid material. The solids form a film on the surface of the emulsion droplets; this steric hindrance inhibits the coalescence of the emulsion (Pickering, 1907). Clay minerals are excellent solid stabilizers, even small fractions (~0.5 wt %) of clay are sufficient for a stable emulsification. Generally, smaller droplets are formed with higher clay fractions (Figure 5.6). Bench-scale studies with kaolin and bentonite showed that bentonite readily formed stable o/w emulsions, while no significant emulsification was achieved with kaolin (Fjordbøge et al., **II**; Gerlot et al., 1984).

The importance of the formation of Pickering emulsions for the ZVI-Clay soil mixing technology is still relatively unknown as no decisive studies have been carried out on the topic. Source zone remediation is expected to benefit from the increased DNAPL-water interface obtained by emulsification. Hence, the source mass depletion may be faster with the addition of an emulsifying clay. Fjordbøge et al. (**II**) found a slightly faster degradation of chlorinated solvents (CT and TCE) in reactors mixed with bentonite compared to reactors mixed with kaolin or no clay. The effect was only observed for reactors with high initial concentrations; whether this was a result of emulsification was not determined.

The conducted investigations showed that bentonite is superior to kaolin for all of the pertinent processes of the ZVI-Clay soil mixing technology. The superior characteristics have been demonstrated with regard to drilling fluid properties, reduction of hydraulic conductivity, and the possible formation of Pickering emulsions. Kaolin was originally used for the early field applications, while all the later applications have utilized bentonite (Fjordbøge et al., **II**). Swelling clays other than bentonite may be used. However, the testing of alternative swelling clays was not found to be particularly desirable as bentonite is readily available and already used as an additive for drilling fluids.

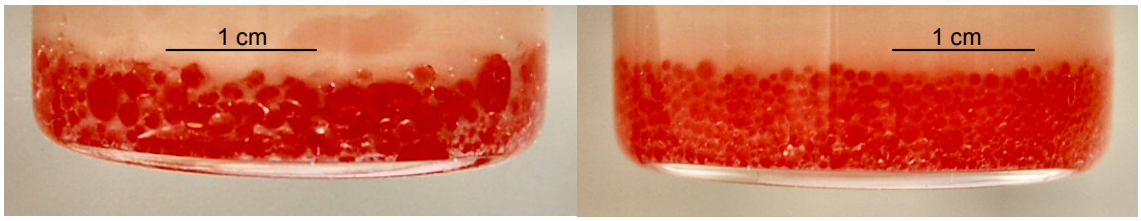

Figure 5.6. Formation of a Pickering o/w emulsion between water and PCE (30 vol %) with (left) 0.5 wt % bentonite and (right) 1.0 wt % bentonite. Red color (Sudan) was added for better visibility of the o/w emulsion (from Fjordbøge et al., **II**).

5.4 Down-gradient effects

The ZVI-Clay technology is hypothesized to reduce the down-gradient mass discharge by changes to both the hydraulic properties and the chemical properties of the source zone. The mass discharge reduction accompanying the extensive source mass depletion has therefore been investigated. A meticulous study on the changes to the down-gradient mass discharge and the relationship with source mass depletion has only been done on one occasion (Fjordbøge et al., **III**, **IV**). However, groundwater concentrations have been monitored in connection with a few other field applications (Bozzini et al., 2006; Fjordbøge et al., **II**; Ovbey et al., 2010).

5.4.1 Down-gradient mass discharge

Investigations on the changes to the mass discharge at a down-gradient control plane (with multilevel samplers) following application of ZVI-Clay soil mixing show several distinct phases throughout the monitoring period (Fjordbøge et al., **IV**). The identified mass discharge phases include: 1) baseline; 2) initial rapid reduction; 3) temporary stagnation or increase; and 4) slower long-term reduction (Figure 5.7). Overall the mass discharge of the parent compound is significantly reduced at the down-gradient control plane (Fjordbøge et al., **IV**), as hypothesized for the remediation technology.

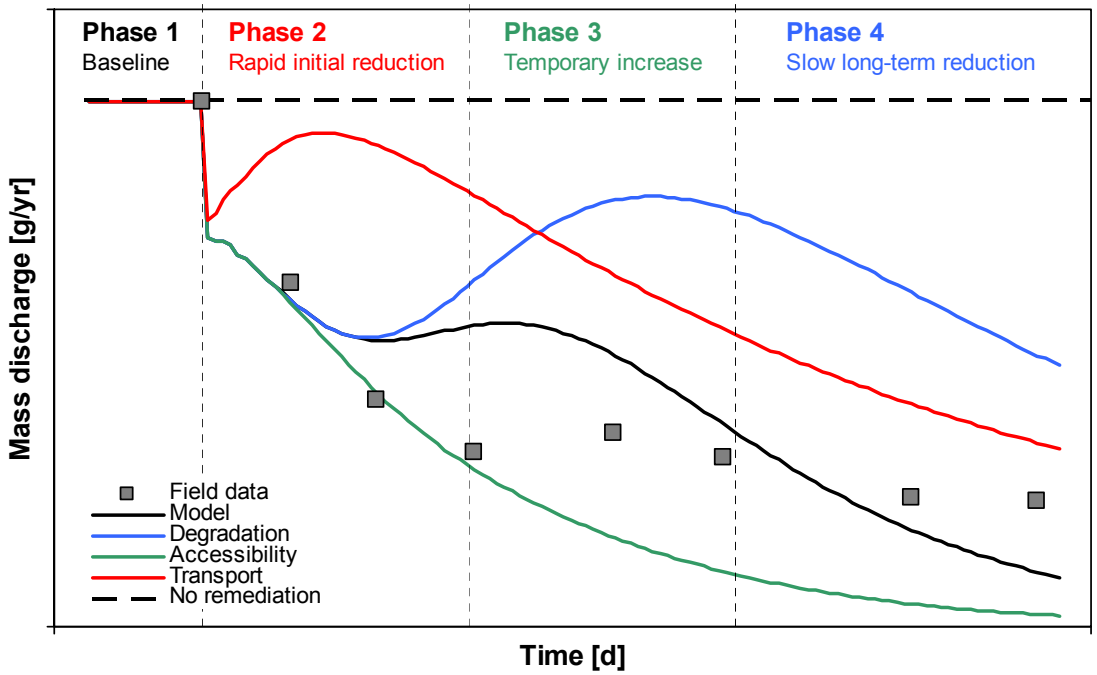

Figure 5.7. The four phases of mass discharge development at a down-gradient control plane in connection with ZVI-Clay soil mixing of a PCE source zone. The illustration includes: Field data (■); a scenario without remediation (dashed line); the modeled baseline scenario (black); a scenario without degradation (blue), a scenario without changes to the contaminant accessibility (green), and a scenario with fast solute transport (red) (modified from Fjordbøge et al., **IV**).

The first phase of mass discharge represents the baseline conditions preceding the application of ZVI-Clay soil mixing. These conditions are the result of the dissolution processes and the natural attenuation in the source zone area. Without an extensive natural attenuation the conditions are relatively stable during a shorter time period.

The most rapid mass discharge reduction occurred in the second phase, which followed immediately after the implementation of ZVI-Clay soil mixing (Figure 5.7). The soil mixing and the addition of bentonite clay caused the hydraulic properties of the source zone to change (Fjordbøge et al., **II**, **IV**). As the groundwater bypassed the soil mixed source zone the hydraulic gradient changed. The hydraulic gradient was reduced at the central, most contaminated part of the down-gradient plume; this resulted in an immediate mass discharge reduction (Fjordbøge et al., **IV**).

The changes to the mass discharge following the initial rapid reduction due to the changed hydraulic properties depended on the site specific conditions and the efficiency of the source mass depletion. These factors will result in the third mass discharge phase, which may either consist of a temporary increase, a temporary stagnation, or a continued reduction of the mass discharge (Figure 5.7). The temporary increase in the down-gradient mass discharge (or concentrations) has been observed for the field applications of ZVI-Clay soil mixing with more detailed down-gradient groundwater monitoring programs (Bozzini et al., 2006; Fjordbøge et al., **IV**; Ovbey et al., 2010).

The temporary increase is linked to the accessibility of the contaminant following ZVI-Clay soil mixing. Before the soil mixing the contaminant (DNAPL) is likely confined primarily to low-accessible lateral pools. The accessibility of the contaminant is likely to increase with the dispersion resulting from the soil mixing process. The more profound the increased accessibility, the more profound the temporary increase of the third mass discharge phase. In case the accessibility of the contaminant is not altered significantly, the third mass discharge phase may be omitted (accessibility scenario, Figure 5.7). This scenario could be valid if: no free phase DNAPL is present in the source zone; the sorption is extensive; or the outer perimeter of the treated area has low contaminant concentrations (Fjordbøge et al., **III**, **IV**), whereby the perimeter may function as a low-permeable barrier between the heavily contaminated center of the source zone and the bypassing groundwater. The concentration gradient at the boundaries of the low-permeable source zone is the driver of the down-gradient mass discharge. Hence, the changes to the down-gradient mass discharge depend on the source mass depletion rate and the solute transport along the source zone boundary. These factors will be determining for the onset, magnitude and duration of the potential temporary increase of the mass discharge. Without an efficient source mass depletion the magnitude and duration

of the third phase will be prolonged as the contaminant will continue to leach into the aquifer (degradation scenario, Figure 5.7), while an efficient source mass depletion will have the opposite effect on the magnitude and duration of the third phase. The solute transport along the boundary of the source zone will be the main determining factor for the onset of the third phase at the down-gradient control plane (transport scenario, Figure 5.7).

The fourth mass discharge phase represents the final stage. At this stage most of the mass in the source zone has already been depleted, whereby the remaining concentration gradient will be low. This will result in a slower long-term reduction of the mass discharge. The long-term mass discharge reduction can also be affected by residual contamination left after the heavily contaminated source zone has been remediated; this contamination could for instance be the result of insufficient source zone characterization.

5.4.2 Relationship between mass depletion and mass discharge

The assessment of the relationship between the source mass depletion and the mass discharge can be done as either a time-continuous analysis or more simply as an end-point analysis. For the ZVI-Clay soil mixing technology, the source mass depletion has normally been determined, while limited data are available on the dissolved down-gradient contamination. Analysis on the relationship between source mass depletion and mass discharge (or groundwater concentration) has been carried out using a simple analytical power law model (eq. 2.3). End-point analysis has been applied for the field data collected after approximately one year of monitoring (Table 5.1; Fjordbøge et al., **II**). A time-continuous analysis of the source mass depletion and mass discharge could only be made on one occasion (Fjordbøge et al., **IV**); this result did not differ significantly from the corresponding end-point analysis.

Overall the analysis showed that the values for the relationship parameter (Γ) between the source mass depletion and the mass discharge was close to one (a linear relationship); an average value of 0.8 [0.3-1.9] was determined.

The overall relationship between the source mass depletion and the mass discharge for the ZVI-Clay soil mixing technology does not differ significantly from other efficient *in situ* remediation technologies (chapter 2.3). However, the relationship parameter is more consistently below one. A low relationship parameter is often associated with source zones where the contaminant mass is located in high-permeability zones (Falta et al., 2005; Falta, 2008), and in some studies the relationship parameter seems to be more dependent on the site specific conditions than the applied *in situ* remediation technology (DiFilippo & Brusseau, 2008; McGuire et al., 2006). The consistently low relationship parameters for the ZVI-Clay soil mixing technology seem suitable when considering the major alteration of the source zone architecture due to soil

mixing; this will in general increase accessibility of the contaminants and make the technology less depended on the preexisting subsurface conditions.

With the four identified phase of mass discharge, a multi-step function may better represent the relationship between source mass depletion and mass discharge reduction. Especially, the second phase with a significant immediate mass discharge reduction, until the efficient source mass depletion becomes dominant, is not well-represented by the simple power law model. In this phase the relationship parameter is expected to be above one, with a significant short-term benefit to the down-gradient receptors. The simple power law model is best suitable for describing the longer-term overall relationship.

5.5 Limitations of ZVI-Clay soil mixing

The ZVI-Clay soil mixing technology has some technological limitations. These include infrastructural challenges at the field sites, the formation of undesirable degradation products, and the post-mixing soil strength.

5.5.1 Infrastructure and accessibility

The infrastructural challenges limit the number of sites where ZVI-Clay soil mixing potentially can be implemented. The technology can be used in various geological settings (Fjordbøge et al., **II**), but requires the soils to be mixable and accessible. The technology requires the removal or re-routing of any subsurface installations or other obstacles. The technology also requires accessibility to the contaminated source zone with the large machinery generally used for the soil mixing process. Smaller machinery can be used but is expected to limit the homogenization efficiency. However, the smaller machinery has lower mobilization costs, which makes it more feasible for small sites (<1000 m^3). For the larger more efficient machinery larger target volumes are required for the technology to be cost-efficient (Table 5.1). The unit cost is generally around 60-230 $/$m^3$, which is comparable to the other aggressive *in situ* remediation technologies (Table 3.1). The ZVI-Clay technology especially has the potential of being very cost-efficient at large source zone. However, which technology is most cost-efficient will depend on site specific conditions.

The infrastructural limitations are not unique to the ZVI-Clay soil mixing technology but also apply to other non-injection based technologies. For source zone areas with low accessibility due to buildings or subsurface installations injection based technologies may be preferable.

5.5.2 Degradation products

Technologies based on the transformation of contaminants to benign end products have common issues regarding the formation of undesirable intermediates. For the degradation of chlorinated solvents (ethenes) with ZVI-

based technologies the formation of more toxic intermediates often focuses on the carcinogenic VC (Table 2.1). As described earlier (Figure 3.1), the formation of VC is not the abiotically preferred degradation pathway for the chlorinated ethenes. Studies on ZVI-Clay soil mixing have shown that ethene and to a minor extent ethane are the favored end products in both bench-scale studies (Fjordbøge et al., **II**) and under field conditions (Fjordbøge et al., **III**). However, under field conditions, the concentrations of the sequential hydrogenolysis products (cDCE and VC) have been observed to increase in the down-gradient groundwater (Fjordbøge et al., **IV**). The increased concentrations were found to decrease again over time, and were most likely the result of natural degradation at the site. However, the relatively strong correlation between iron corrosion and favorable condition for biotransformation is still worth keeping in mind. The issue of undesirable degradations products is not limited to the ZVI-Clay soil mixing technology; it applies to the ZVI technologies in general.

5.5.3 Soil strength

Depending on the plans for site restoration and future use of the site, the post-mixing soil strength may be a limiting factor for application of the ZVI-Clay soil mixing technology. Traditionally, soil mixing was used for soil stabilization. Unfortunately, the simultaneous addition of reactive ZVI and cement, which is used for soil stabilization, inhibits the source mass depletion. Bench-scale studies have shown that even small fractions of cement (<1 %) prevents the development of reduced conditions, and decrease the contaminant degradation rate. The degradation process can be completely discontinued with the large fraction of cement (e.g., 8 %) normally used for soil stabilization (Fjordbøge et al., **II**).

The soil mixing process, without the addition of cement, reduces the soil strength in the source zone. Self-weigh consolidation is a slow process. A study on the development in undrained shear soil strengths (peak) without any soil strengthening initiatives showed that the consolidation process was very slow (Figure 5.8). Only the bottom 1-1.5 m of the mixed source zone was returned to strengths above 250 kN/m^2 within 23 months (Fjordbøge et al., **III**). The process is not expected to return the soils to their pre-mixing strength within a reasonable time period. Additional soil strengthening initiatives are needed in connection with site closure.

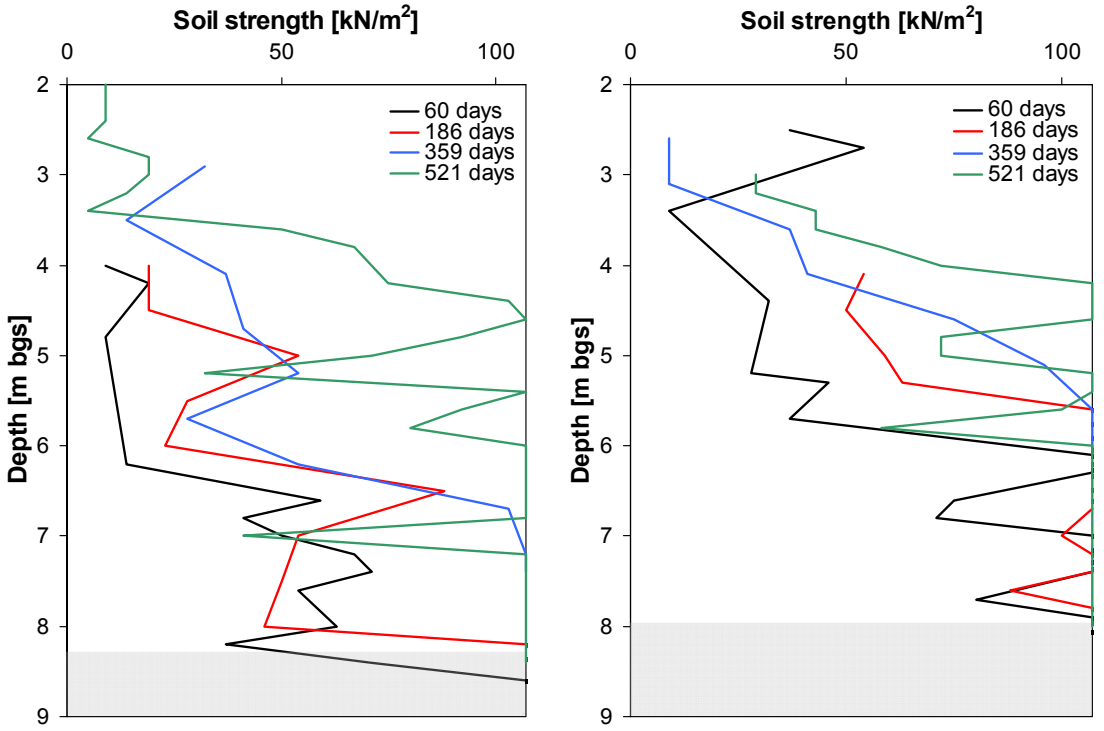

Figure 5.8. Changes in the undrained shear soil strength (peak) at two points in the mixed source zone. Results for 2, 6, 12, and 18 months after the implementation of ZVI-Clay soil mixing; no soil strengthening initiatives have been applied. The applied vane tests could only measure up to 107 kN/m^2. The shaded area represents the intact clay till underneath the source zone area (from Fjordbøge et al. **III**).

Site restoration subsequent to source zone remediation with ZVI-Clay soil mixing has thus far been limited to undeveloped land use and paving of the area. The soil strength issue has thus far been resolved by either back-filling with soil materials and geotextiles (Fjordbøge et al., **III**; Ovbey et al., 2010), or the addition of cement to the topmost 1.5 m of the soil mixed area (Bozzini et al., 2006; Shackelford et al., 2005). The back-filling has been combined with either the placement of a surcharge on the area after soil mixing was finalized (Ovbey et al., 2010), or preceding self-weight consolidation (Fjordbøge et al., **III**). These approaches are suitable for the planned post-mixing land use at these sites; however, whether it is sufficient for opening the sites to more general land use is unknown. It would be desirable to identify a more inert agent (e.g., a polymer) for efficient soil stabilization, which could be added during the ZVI-Clay soil mixing process without inhibitory effects on the source mass depletion.

6 Conclusions

Contaminated source zones act as the driver of down-gradient mass discharge to vulnerable receptors; this is a concern at numerous sites worldwide. Efficient source mass depletion and protection of the down-gradient receptors are areas of great interest. *In situ* remediation technologies show varying degrees of efficiency with regard to source mass depletion. The remediation technologies are generally susceptible to subsurface heterogeneities, while some also include a risk of inadvertent spreading of the contaminants. In this thesis the potential of aggressive ZVI technologies for *in situ* remediation of chlorinated solvent source zones and the possible down-gradient effects were investigated. The investigation was based partly on an elaborate review of the nZVI technology and in particular on the conducted bench-scale studies and field applications of the emerging ZVI-Clay soil mixing technology.

In general, the ZVI technologies for source remediation were efficient at degrading an array of chlorinated solvents (methanes, ethanes and ethenes), while producing only minor amounts of sequential hydrogenolysis intermediates. The degradability and pathways of chlorinated compounds have previously been researched in connection with permeable reactive barriers. The following conclusions will focus on the key findings specific to the two investigated ZVI technologies, nZVI injection and ZVI-Clay soil mixing.

The following conclusions are the outcome of the elaborate review on the nZVI technology:

- The applied nZVI products have diverse characteristics. These are under constant development to achieve better reactivity, mobility and affinity for the contaminants (DNAPL). The various properties are determining for the subsurface fate, the risks, and the remedial benefits of nZVI.

- The fate of the nZVI particles in the subsurface is controlled by the persistency and the mobility of nZVI. Currently, the mobility of nZVI is limited to a few meters beyond the injection point, while the highly reactive particles are rapidly exhausted by oxidation with the abundant electron acceptors in the subsurface. The assessment of subsurface fate is primarily based on bench-scale studies under ideal conditions, and thus associated with some uncertainty. The assessment should be revised with the optimization of the nZVI characteristics.

- The risk assessment of nZVI for field application was based on a high level of ignorance. The fate in the subsurface is uncertain, while the toxicity and bioaccumulation of nZVI are generally unknown. Data

collected so far indicate low toxicity, limited persistency and limited mobility. Hence, no severe apparent risks were identified.

- The few reported field applications of nZVI were found to significantly decrease groundwater concentrations of chlorinated solvents. However, the efficiency of the applications varied significantly and a rebound in groundwater concentrations was a general problem at the sites. This place nZVI in the same category as other injection based remediation technologies, which are vulnerable to subsurface heterogeneities and insufficient contact with the contaminant. The technology appears to be most applicable for contaminated plumes or homogeneous source zones with relatively low contaminant concentrations. Several reinjections are likely required for sufficient source mass depletion. Due to the injection based contact limitations and the rapid exhaustion of the injection nZVI, remediation of DNAPL does not presently seem feasible.

The following conclusions are the outcome of the experimental research based on bench-scale studies and field applications of the ZVI-Clay soil mixing technology:

- The removal efficiencies with the ZVI-Clay soil mixing technology were generally high for contaminated source zones. The technology was capable of depleting high concentrations of contaminants (DNAPL) below given soil quality criteria. The remediation efficiency was above 80 % at all the source zone; most sites showed a source mass reduction of around two orders of magnitude.

- A superior drilling fluid was obtained using bentonite clay compared to kaolin clay; this is due to the swelling properties of bentonite. Bench-scale studies showed that bentonite produced superior drilling fluid properties, hydraulic conductivity reduction, and DNAPL emulsification.

- Soil mixing did not result in complete homogenization; however, the conditions were considerably more uniform after the soil mixing process. Especially, horizontal homogenization was limited; this may be utilized to optimize the remedial design. The vertical homogenization of the ZVI, the contaminants, and the encountered geological layers depended on the soil mixing equipment and the choice of method for ZVI addition. Auger mixing with ZVI addition to the drilling fluid gave the most uniform results.

- Remediation with the ZVI-Clay soil mixing technology has resulted in a significant down-gradient mass discharge reduction. The mass discharge depended on the remedial efficiency of the technology and the site

specific conditions. Generally, the source depletion was faster than the related down-gradient mass discharge reduction. The mass discharge was most rapidly reduced immediately after soil mixing due to the changed hydraulic properties of the source zone. A temporary increase in mass discharge may be observed, as the changes to the subsurface by soil mixing can render the contaminant (DNAPL) more accessible to the bypassing groundwater. The temporary increase can be counteracted by: efficient source mass depletion, high sorption, slow solute transport along the boundaries of the mixed source zone, and generally low concentrations at the perimeter of the area.

- The reduced post-mixing soil strength is currently seen as the main limitation of the technology, since it may limit the future land use at the site. The heavy soil mixing machinery limits the number of sites that the technology may be applied to due to site accessibility requirements and high mobilization cost. The remediation by ZVI-Clay soil mixing is not considered feasible for sites with a targeted source zone volume of less than 1000 m^3.

In general, the literature review and the conducted experimental work suggest that both the ZVI technologies can be efficient for remediation of homogeneous source zone without the presence of free phase DNAPL. The two different remediation technologies have each their appropriate niches for field application due to especially the difference in delivery methods and reactive properties. However, for the more heavily contaminated, heterogeneous source zones only ZVI-Clay is currently seen as a feasible remediation technology.

7 Future research

The potential of source zone remediation by ZVI technologies (i.e. nZVI injection and ZVI-Clay soil mixing) has been investigated in this thesis. During the investigations, it became evident that further development within the areas identified below could add to the understanding of the technologies.

- There is a need for more meticulous field studies on the application of both the ZVI technologies. The datasets on which to assess the technologies are still limited; few of the field applications have been done with the intent of a fundamental improvement of the knowledge on source zone remediation and down-gradient risks. The effects of various site specific and technological properties could be clarified with additional field data.

- The toxicity and the subsurface fate of nZVI are generally unknown; this complicates a reliable risk assessment of nZVI application at contaminated sites. Improved monitoring of the nZVI toxicity, mobility, and persistency after source zone injection would benefit the classification of nZVI related risks.

- Optimization of the ZVI-Clay soil mixing technology with regard to the remedial design and the soil mixing equipment has the potential of further improving the vertical homogenization process, reducing down-gradient mass discharge, and making the technology feasible for smaller sites.

- The importance of emulsification during soil mixing is still generally unknown. Bench-scale studies indicate that with the presence of DNAPL emulsification may facilitate source mass depletion. Also, the increased DNAPL-water interface can potentially have an impact on the down-gradient mass discharge. Further investigations on the emulsification process could improve the understanding of the efficient source mass depletion and mass discharge reduction.

- The restoration of ZVI-Clay soil mixing sites is of interest in order to better determine which sites are suitable for remediation. Methods to increase the soil strength should be investigated; an interdisciplinary approach involving the field of geotechnical engineering may be beneficial as soil mixing for years has been used for soil stabilization.

8 References

Allan, A. 2001. Containment landfills: the myth of sustainability. Eng. Geol. 60, 3-19.

Arnold, W.A., Ball, W.P., Roberts, A.L. 1999. Polychlorinated ethane reaction with zero-valent zinc: pathways and rate control. J. Contam. Hydrol. 40, 183-200.

Arnold, W.A., Roberts, A.L. 2000. Pathways and Kinetics of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Fe(0) Particles. Environ. Sci. Technol. 34, 1794-1805.

Auffan, M., Achouak, W., Rose, J., Roncato, M.A., Chanéac, C.,Waite, D.T., Masion, A., Woicik, J.C., Wiesner, M.R., Bottero, J.Y. 2008. Relation between the redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*. Environ. Sci. Technol. 42, 6730–6735.

Bahr, J.M. 1989. Analysis of Nonequilibrium Desorption of Volatile Organics during Field Test of Aquifer Decontamination. J. Contam. Hydrol. 4, 205-222.

Basu, N.B., Fure, A.D., Jawitz, J.W. 2008. Simplified contaminant source depletion models as analogs of multiphase simulators. J. Contam. Hydrol. 97, 87-99.

Basu, N.B., Rao, P.S.C., Poyer, I.C., Annable, M.D., Hatfield, K. 2006. Flux-based assessment at a manufacturing site contaminated with trichloroethylene. J. Contam. Hydrol. 86, 105-127.

Baun, A., Sørensen, S.N., Rasmussen, R.F., Hartmann, N.B., Koch, C.B. 2008. Toxicity and bioaccumulation of xenobiotic organic compounds in the presence of aqueous suspensions of aggregates of nano-C60. Aquat. Toxicol. 86, 379-387.

Bennett, P., He, F., Zhao, D., Aiken, B., Feldman, L. 2010. In situ testing of metallic iron nanoparticle mobility and reactivity in a shallow granular aquifer. J. Contam. Hydrol. 116, 35-46.

Berge, N.D., Ramsburg, C.A. 2009. Oil-in-Water Emulsions for Encapsulated Delivery of Reactive Iron Particles. Environ. Sci. Technol. 43, 5060-5066.

Borchardt, J.K., 2010. Avoiding the Blowout. Mech. Eng. 132, 40-41.

Bozzini, C., Simpkin, T., Sale, T., Hood, D., Lowder, B. 2006. DNAPL Remediation at Camp Lejeune Using ZVI-Clay Soil Mixing. Proceedings: The Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2006, Monterey, California.

Brandes, D., Farley, K.J. 1993. Importance of Phase Behavior on the Removal of Residual DNAPLs from Porous Media by Alcohol Flooding. Water Environ. Res. 65, 869-878.

Brooks, M.C., Annable, M.D., Suresh, P., Rao, C., Hatfield, K., Jawitz, J.W., Wise, W.R., Wood, A.L., Enfield, C.G. 2004. Controlled release, blind test of DNAPL remediation by ethanol flushing. J. Contam. Hydrol. 69, 281-297.

Brooks, M.C., Wood, A.L., Annable, M.D., Hatfield, K., Cho, J., Holbert, C., Rao, P.S.C., Enfield, C.G., Lynch, K., Smith, R.E.. 2008. Changes in contaminant mass discharge from DNAPL source mass depletion: Evaluation at two field sites. J. Contam. Hydrol. 102, 140-153.

Brusseau, M.L., Nelson, N.T., Zhang, Z., Blue, J.E., Rohrer, J., Allen, T. 2007. Source-zone characterization of a chlorinated-solvent contaminated Superfund site in Tucson, AZ. J. Contam. Hydrol. 90, 21-40.

Buettner, H.M., Daily, W.D. 1995. Cleaning Contaminated Soil Using Electrical Heating and Air Stripping. J. Environ. Eng. 121, 580-589.

Chang, P.R., Pantaleoni, A.D., Shenk, D.J. 2010. Jet-Assisted Injection of Nano-Scale, Zero-Valent Iron Treat TCE in a Deep Alluvial Aquifer. Proceedings: The Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2010, Monterey, California.

Chapman, S.W., Parker, B.L. 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. Water Resour. Res. 41, W12411.

Chen, G, Hoag, G.E., Chedda, P., Nadim, F., Woody, B.A., Dobbs, G.M. 2001. The mechanism and applicability of in situ oxidation of trichloroethylene with Fenton's reagent. J. Hazard. Mater. B87, 171-186.

Choe, S., Lee, S.-H., Chang, Y.-Y., Hwang, K.-Y., Khim, J. 2001. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe^0. Chemosphere 42, 367-372.

Chown, J.C., Kueper, B.H., McWhorter, D.B. 1997. The Use of Upward Hydraulic Gradients to Arrest Downward DNAPL Migration in rock Fractures. Ground Water 35, 483-491.

Cullen, L.G., Tilston, E.L., Mitchell, G.R., Collins, C.D., Shaw, L.J. 2011. Assessing the impact of nano- and micro-scale zerovalent iron particles on soil microbial activities: Particle reactivity interferes with assay conditions and interpretation of genuine microbial effects. Chemosphere 82, 1675-1682.

Dahmani, M.A., Huang, K., Hoag, G.E. 2006. Sodium persulfate oxidation for the remediation of chlorinated solvents (USEPA superfund innovative technology evaluation program). Water Air Soil Pollut. Focus 6, 127-141.

DiFilippo, E.L., Brusseau, M.L. 2008. Relationship between mass-flux reduction and source-zone mass removal: Analysis of field data. J. Contam. Hydrol. 98, 22-35.

DK EPA. 2010a. Redegørelse om jordforurening 2008 [Report on soil contamination 2008]. Report no. 1 2010, Danish Environmental Protection Agency, Ministry of the Environment (in Danish).

DK EPA. 2010b. Liste over kvalitetskriterier i relation til forurenet jord og kvalitetskriterier for drikkevand [List of quality criteria in relation to contaminated soil and quality criteria for drinking water]. Danish Environmental Protection Agency, Ministry of the Environment (In Danish). Updated July 2010, Accessed January 20th 2011 at: http://www.mst.dk/NR/rdonlyres/2EED6D00-3C69-486A-BED8-34B1FD527A8D/0/Kvalitets kriterierjord_og_drikkevandfinaljuniogjuli2010.doc

Doherty, R.E. 2000a. A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 1–Historical Background; Carbon Tetrachloride and Tetrachloroethylene. J. Environ. Forensics 1, 69-81.

Doherty, R.E. 2000b. A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 2–Trichloroethylene and 1,1,1-Trichloroethane. J. Environ. Forensics 1, 83-93.

CSU. 2007. Source Zone Remediation via ZVI-Clay. Brochure from Center for Contaminant Hydrology, Colorado State University. Accessed March 1st 2011 at: http://www.engr.colostate.edu/CCH/Brochure-ZVI-Clay%2011-07.pdf

EC. 2006. Soil protection – The story behind the Strategy. Office for Official Publications of the European Communities, European Commission.

Edstrom, J.A., Semmens, M.J., Hozalski, R.M., Clapp, L.W., Novak, P.J. 2005. Stimulation of Dechlorination by Membrane-Delivered Hydrogen: Small Field Demonstration. Environ. Eng. Sci. 22, 281-293.

Edwards, D.A., Little, J.W., Lanik, W., Hajali, P.A. 2002. Calibration of a Model for Volatile Organic Compound Mass Removal by Multiphase Extraction. J. Environ. Eng. 128, 472-475.

Einarson, M.D., Mackay, D.M. 2001. Predicting impacts of groundwater contamination. Environ. Sci. Technol. 35, 66-73

Elliott, D.W., Zhang, W.-X. 2001. Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment. Environ. Sci. Technol. 35, 4922-4926.

Elsner, M., Couloume, G.L., Mancini, S., Burns, L., Lollar, B.S. 2010. Carbon Isotope Analysis to Evaluate Nanoscale Fe(0) Treatment at a Chlorohydrocarbon Contaminated Site. Ground Water Monit. Rem. 30, 79-95.

Falta, R.W. 2008. Methodology for Comparing Source and Plume Remediation Alternatives. Ground Water 46, 272-285.

Falta, R.W., Rao, P.S., Basu, N. 2005. Assessing the impacts of partial mass depletion in DNAPL source zones I. Analytical modeling of source strength functions and plume response. J. Contam. Hydrol. 78, 259-280.

Field, J.A., Sierra-Alvarez, R. 2004. Biodegradability of chlorinated solvents and related chlorinated aliphatic compounds. Rev. Environ. Sci. BioTechnol. 3, 185-254.

Fjordbøge, A.S., Kjeldsen, P. 2008. Assessment of Zero-Valent Iron Technologies for Source Remediation of Organophosphorous Insecticides. Proceedings: The Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2008, Monterey, California.

Fountain, J.C., Klimek, A., Beikirch, M.G., Middleton, T.M. 1991. The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer. J. Hazard. Mater. 28, 295-311.

Freeze, R.A., McWhorter, D.B. 1997. A Framework for Assessing Risk Reduction Due to DNAPL Mass Removal fom Low-Permeability Soils. Ground Water 35, 111-123.

Friis, A.K. 2006. The potential for reductive dechlorination after thermal treatment of TCE-contaminated aquifers. PhD Thesis, Institute of Environment & Resources, Technical University of Denmark.

Gates, D.D., Siegrist, R.L. 1995. In-Situ Chemical Oxidation of Trichloroethylene Using Hydrogen Peroxide. J. Environ. Eng. 121, 639-644.

Gavaskar, A.R. 1999. Design and construction techniques for permeable reactive barriers. J. Hazard. Mater. 68, 41-71.

Gelot, A., Friesen, W., Hamza, H.A. 1984. Emulsification of Oil and Water in the Presence of Finely Divided Solids and Surface-Active Agents. Colloids Surf. 12, 271-303.

Gillham, R.W., O'Hannesin, S.F. 1994. Enhanced degradation of Halogenated Aliphatics by Zero-Valent Iron. Ground Water 32, 958-967.

Glazier, R., Venkatakrishnan, R., Gheorghiu, F., Walata, L., Nash, R., Zhang, W.-X. 2003. Nanotechnology takes root. Civil Eng. 73, 64-69.

Gordon, M.J. 1998. Case History of a Large-Scale Air Sparging/Soil Vapor Extraction System for Remediation of Chlorinated Volatile Organic Compounds in Ground Water. Ground Water Monit. Remediat. 18, 137-149.

Grim, R.E. 1962. Clay Mineralogy. Science 135, 890-898.

Guilbeault, M.A., Parker, B.L., Cherry, J.A. 2005. Mass and Flux Distributions from DNAPL Zones in Sandy Aquifers. Ground Water 43, 70-86.

Hains, S., Millette, D., Gosselin, S., Boutin, A., Barbeau, M. 2008. Implementation of a Nanoscale Zero-Valent Iron Diffuse Reactive Zone for Treatment of TCE in a Deep Aquifer, Quebec City, Canada. Proceedings: The Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2008, Monterey, California.

Hansen, S.F., Maynard, A., Baun, A., Tickner, J.A. 2008. Late lessons from early warnings for nanotechnology. Nat. Nanotechnol. 3, 444-447.

Harkness, M.R., Bracco, A.A., Brennan, Jr., M.J., Deweerd, K.A., Spivack, J.L. 1999. Use of Bioaugmentation To Stimulate Complete Reductive Dechlorination of Trichloroethene in Dover Soil Columns. Environ. Sci. Technol. 33, 1100-1109.

Hartmann, N.B., Von der Kammer, F., Hofmann, T., Baalousha, M., Ottofuelling, S., Baun, A. 2010. Algal testing of titanium dioxide nanoparticles—Testing considerations, inhibitory effects and modification of cadmium bioavailability. Toxicology 269, 190-197.

Haselow, J.S., Siegrist, R.L., Crimi, M., Jarosch, T. 2003. Estimating the Total Oxidant Demand for *In Situ* Chemical Oxidation Design. Remediation 13, 5-16.

Hatfield, K., Annableb, M., Cho, J., Rao, P.S.C., Klammler, H. 2004. A direct passive method for measuring water and contaminant fluxes in porous media. J. Contam. Hydrol. 75, 155-181.

He, F., Zhang, M., Qian, T., Zhao, D. 2009. Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: Column experiments and modeling. J. Colloid Interface Sci. 334, 96-102.

He, F., Zhao, D. 2005. Preparation and Characterization of a New Class of Starch-Stabilized Bimetallic Nanoparticles for Degradation of Chlorinated Hydrocarbons in Water. Environ. Sci. Technol. 39, 3314-3320.

He, F., Zhao, D., Liu, J., Roberts, C.B. 2007. Stabilization of Fe-Pd Nanoparticles with Sodium Carboxymethyl Cellulose for Enhanced Transport and Dechlorination of Trichloroethylene in Soil and Groundwater. Ind. Eng. Chem. Res. 46, 29-34.

He, F., Zhao, D., Paul, C. 2010. Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. Water Res. 44, 2360-2370.

Heimann, A.C., Friis, A.K., Jakobsen, R. 2005. Effects of sulfate on anaerobic chloroethene degradation by an enriched culture under transient and steady-state hydrogen supply. Water Res. 39, 3579-3586.

Henderson, A.D., Demond, A.H. 2007. Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review. Environ. Eng. Sci. 24, 401-423.

Henn, K.W., Waddill, D.W. 2006. Utilization of Nanoscale Zero-Valent Iron for Source Remediation—A Case Study. Remediation 16, 57-77.

Heron, G., Carroll, S., Nielsen, S.G. 2005. Full-Scale Removal of DNAPL Constituents Using Steam-Enhanced Extraction and Electrical Resistance Heating. Ground Water Monit. Remediat. 25, 92-107.

Heron, G., Parker, K., Galligan, J., Holmes, T.C. 2009. Thermal Treatment of Eight CVOC Source Zones to Near Nondetect Concentrations. Ground Water Monit. Remediat. 29, 56-65.

Heron, G., Van Zutphen, M., Christensen, T.H., Enfield, C.G. 1998. Soil Heating for Enhanced Remediation of Chlorinated Solvents: A Laboratory Study on Resistive Heating and Vapor Extraction in a Silty, Low-Permeable Soil Contaminated with Trichloroethylene. Environ. Sci. Technol. 32, 1474-1481.

IARC. 2010. The International Agency for Research on Cancer. Agents Classified by the IARC Monographs, Volumes 1–100. Updated August 2010. Accessed January 17th 2011 at: http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf.

Jawitz, J.W., Fure, A.D., Demmy, G.G., Berglund, S., Rao, P.S.C. 2005. Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction. Water Resour. Res. 41, W10408.

Jawitz J.W., Sillan, R.K., Annable, M.D., Suresh, P., Rao, C., Warner, K. 2000. In-Situ Alcohol Flushing of a DNAPL Source Zone at a Dry Cleaner Site. Environ. Sci. Technol. 34, 3722-3729.

Johnson, R.L., Johnson, P.C., McWhorter, D.B., Hinchee, R.E., Goodman, I. 1993. An Overview of In Situ Air Sparging. Ground Water Monit. Remediat. 13, 127-135.

Jørgensen, I.V. 2008. Simulation of Mass Flux and Mass Removal from a Contaminated Site to Groundwater. MSc Thesis, Department of Environmental Engineering, Technical University of Denmark.

Kaplan, A.R., Munakata-Marr, J., Illangasekare, T.H. 2008. Biodegradation of Residual Dense Nonaqueous-Phase Liquid Tetrachloroethene: Effects on Mass Transfer. Biorem. J. 12, 21-31.

Kaslusky, S.F., Udell, K.S. 2002. A theoretical model of air and steam co-injection to prevent the downward migration of DNAPLs during steam-enhanced extraction. J. Contam. Hydrol. 55, 213-232.

Kim, H.-J., Phenrat, T., Tilton, R.D., Lowry, G.V. 2009. Fe^0 Nanoparticles Remain Mobile in Porous Media after Aging Due to Slow Desorption of Polymeric Surface Modifiers. Environ. Sci. Technol. 43, 3824-3830.

Kjeldsen, P., Christensen, T.H. 1996. Kemiske stoffers opførsel i jord og grundvand: Bind 2 [Behavior of chemical substances in soil and groundwater: Volume 2]. Environmental Project No. 20, Danish Environmental Protection Agency, Ministry of the Environment (in Danish).

Krembs, F.J., Siegrist, R.L., Crimi, M.L., Furrer, R.F., Petri, B.G. 2010. ISCO for Groundwater Remediation: Analysis of Field Applications and Performance. Ground Water Monit. Remediat. 30, 42-53.

Kübert, M., Finkel, M. 2006. Contaminant mass discharge estimation in groundwater based on multi-level point measurements: A numerical evaluation of expected errors. J. Contam. Hydrol. 84, 55-80.

Kueper, B.H., Redman, D., Starr, R.C., Reitsma, S., Mah, M. 1993. A Field Experiment to Study the Behavior of Tetrachloroethylene Below the Water Table: Spatial Distribution of Residual and Pooled DNAPL. Ground Water 31, 756-766.

Lampron, K.J., Chiu, P.C., Cha, D.K. 2001. Reductive Dehalogenation of Chlorinated Ethenes with Elemental Iron: The Role of Microorganisms. Wat. Res. 35, 3077-3084.

Larsson, S. 2005. State of Practice Report – Execution, monitoring and quality control. Volume 2: State of Practice Reports. Proceedings from the International Conference on Deep Mixing '05, May, 2005, Stockholm, Sweden.

Lee, C., Kim, J.Y., Lee, W.I., Nelson, K.L., Yoon, J., Sedlak, D.L. 2008. Bactericidal effect of zero-valent iron nanoparticles on *escherichia coli*. Environ. Sci. Technol. 42, 4927-4933.

Lendvay, J.M., Löffler, F.E., Dollhopf, M., Aiello, M.R., Daniels, G., Fathepure, B.Z., Gebhard, M., Heine, R., Helton, R., Shi, J., Krajmalnik-Brown, R., Major, Jr. C.L., Barcelona, M.J., Petrovskis, E., Hickey, R., Tiedje, J.M., Adriaens, P. 2003. Bioreactive Barriers: A Comparison of Bioaugmentation and Biostimulation for Chlorinated Solvent Remediation. Environ. Sci. Technol. 37, 1422-1431.

Li, L., Fan, M., Brown, R.C., Wang, J., Wang, W., Song, Y., Zhang, P. 2006. Synthesis, Properties, and Environmental Applications of Nanoscale Iron-Based Materials: A Review. Crit. Rev. Environ. Sci. Tech. 36, 405-431.

Li, K.B., Goovaerts, P., Abriola, L.M. 2007. A geostatistical approach for quantification of contaminant mass discharge uncertainty using multilevel sampler measurements. Water Resour. Res. 43, W06436.

Li, Z., Greden, K., Alvarez, P., Gregory, K., Lowry, G. 2010. Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zero-valent iron (nZVI) to E. coli. Environ. Sci. Technol. 44, 3462-3467.

Li, H., Zhou, Q., Wu, Y., Fu, J., Wang, T., Jiang, G. 2009. Effects of waterborne nano-iron on medaka (oryzias latipes): antioxidant enzymatic activity, lipid peroxidation and histopathology. Ecotoxicol. Environ. Saf. 72, 684-692.

Lien, H.-L., Zhang, W.-X. 1999. Transformation of Chlorinated Methanes by Nanascale Iron Particles. J. Environ. Eng. 125, 1042-1047.

Lien, H.-L., Zhang, W.-X. 2001. Nanoscale iron particles for complete reduction of chlorinated ethenes. Colloids Surf. A 191, 97-105.

Lien, H.-L., Zhang, W.-X. 2005. Hydrodechlorination of Chlorinated Ethanes by Nanoscale Pd/Fe Bimetallic Particles. J. Environ. Eng. 131, 4-10.

Lin, Y., Skaff, H., Emrick, T., Dinsmore, A.D., Russell, T.P. 2003. Nanoparticle Assembly and Transport at Liquid-Liquid Interfaces. Science 299, 226-229.

Liu, C., Ball, W.P. 2002. Back Diffusion of Chlorinated Solvent Contaminants from a Natural Aquitard to a Remediated Aquifer Under Well-Controlled Field Conditions: Predictions and Measurements. Ground Water 40, 175-184.

Liu, Y., Lowry, G.V. 2006. Effect of Particle Age (Fe^0 Content) and Solution pH On NZVI Reactivity: H_2 Evolution and TCE Dechlorination. Environ. Sci. Tech. 40, 6085-6090.

Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S., Lowry, G.V. 2005. TCE Dechlorination Rates, Pathways, and Efficiency of Nanoscale Iron Particles with Different Properties. Environ. Sci. Technol. 39, 1338-1345.

Liu, Y., Phenrat, T., Lowry, G.V. 2007. Effect of TCE Concentration and Dissolved Groundwater Solutes on NZVI-Promoted TCE Dechlorination and H_2 Evolution. Environ. Sci. Technol. 41, 7881-7887.

Liu, J., Shi, B., Jiang, H., Huang, H., Wang, G., Kamai, T. 2011. Research on the stabilization treatment of clay slope topsoil by organic polymer soil stabilizer. Eng. Geol. 117, 114-120.

Londergan, J.T., Meinardus, H.W., Mariner, P.E., Jackson, R.E., Brown, C.L., Dwarakanath, V., Pope, G.A., Ginn, J.S., Taffinder, S. 2001. DNAPL Removal from a Heterogeneous Alluvial Aquifer by Surfactant-Enhanced Aquifer Remediation. Ground Water Monit. Remediat. 21, 57-67.

Lowry, G.V., Johnson, K.M. 2004. Congener-Specific Dechlorination of Dissolved PCBs by Microscale and Nanoscale Zerovalent Iron in a Water/Methanol Solution. Environ. Sci. Technol. 38, 5208-5216.

Mackay, D.M., Cherry, J.A. 1989. Groundwater contamination: Pump-and-treat remediation. Environ. Sci. Technol. 23, 630-636.

Major, D.W., McMaster, M.L., Cox, E.E., Edwards, E.A., Dworatzek, S.M., Hendrickson, E.R., Starr, M.G., Payne, J.A., Buonamici, L.W. 2002. Field Demonstration of Successful Bioaugmentation To Achieve Dechlorination of Tetrachloroethene To Ethene. Environ. Sci. Technol. 36, 5106-5116.

Matheson, L.J., Tratnyek, P.G. 1994. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. Environ. Sci. Technol. 28, 2045-2053.

McDade, J.M., McGuire, T.M., Newell, C.J. 2005. Analysis of DNAPL Source-Depletion Costs at 36 Field Sites. Remediat. 15, 9-18.

McGuire, T.M., McDade, J.M., Newell, C.J. 2006. Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites. Ground Water Monit. Remediat. 26, 73-84.

Moore, M.N. 2006. Do nanoparticles present ecotoxicological risks for the health of the aquatic environment? Environ. Int. 32, 967-976.

Mumford, K.G., Thomson, N.R., Allen-King, R.M. 2005. Bench-Scale Investigation of Permanganate Natural Oxidant Demand Kinetics. Environ. Sci. Technol. 39, 2835-2840.

Nurmi, J.T., Tratnyek, P.G., Sarathy, V., Baer, D.R., Amonette, J.E., Pecher, K., Wang, C., Linehan, J.C., Matson, D.W., Penn, R.L., Driessen, M.D. 2005. Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics. Environ. Sci. Technol. 39, 1221-1230.

Nyer, E.K., Page, G.B. 2004. Treatment Technology: Special Delivery. Ground Water Monit. Remediat. 24, 34-40.

O'Hannesin, S.F., Gillham, R.W. 1998. Long-Term Performance of an In Situ "Iron Wall" for Remediation of VOCs. Ground Water 36, 164-170.

Olson, M.R., Sale, T.C., Shackelford, C.D., Bozzini, C., Skeean, J. (submitted). Chlorinated Solvent Source Zone Remediation via ZVI-Clay Soil Mixing: One-Year Results. Submitted to Ground Water Monit. Remediat.

Ovbey, T.W., Thomson, M.M., Bozzini, C. 2010. In Situ Remediation of Chlorinated Solvent Source Zone Using ZVI-Clay Treatment Technology. Proceedings: The Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2010, Monterey, California.

Parker, B.L., Cherry, J.A., Chapman, S.W., Guiltbeault, M.A. 2003. Review and analysis of chlorinated solvent dense non-aqueous phase liquid distributions in five sandy aquifers. Vadose Zone J. 2, 116-137.

Parker, B.L., McWhorter, D.B., Cherry, J.A. 1997. Diffusive Loss of Non-Aqueous Phase Organic Solvents from Idealized Fracture Networks in Geologic Media. Ground Water 35, 1077-1088.

Parker, J.C., Park, E. 2004. Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. Water Resour. Res. 40, W05109.

PEN. 2011. The Project of Emerging Nanotechnologies. Woodrow Wilson International Center for Scholars, Washington, DC. Accessed February 12th 2011 at: http://www.nanotechproject.org/inventories/remediation_map/

Phenrat, T., Cihan, A., Kim, H.-J., Mital, M., Illangasekare, T., Lowry, G.V. 2010. Transport and Deposition of Polymer-Modified Fe0 Nanoparticles in 2-D Heterogeneous Porous Media: Effects of Particle Concentration, Fe^0 Content, and Coatings. Environ. Sci. Technol. 44, 9086-9093.

Phenrat, T., Kim, H.-J., Fagerlund, F., Illangasekare, T., Tilton, R.D., Lowry, G.V. 2009a. Particle Size Distribution, Concentration, and Magnetic Attraction Affect Transport of Polymer-Modified Fe^0 Nanoparticles in Sand Columns. Environ. Sci. Technol. 43, 5079-5085.

Phenrat, T., Long, T.C., Lowry, G.V., Veronesi, B. 2009b. Partial oxidation ("aging") and surface modification decrease the toxicity of nanosized zerovalent iron. Environ. Sci. Technol. 43, 195-200.

Phillips, D.H., Van Nooten, T., Bastiaens, L., Russell, M.I., Dickson, K., Plant, S., Ahad, J.M.E., Newton, T., Elliot, T., Kalin, R.M. 2010. Ten Year Performance Evaluation of a Field-Scale Zero-Valent Iron Permeable Reactive Barrier Installed to Remediate Trichloroethene Contaminated Groundwater. Environ. Sci. Technol. 44, 3861-3869.

Poulsen, M.M.., Kueper, B.H. 1992. A Field Experiment To Study the Behavior of Tetrachloroethylene in Unsaturated Porous Media. Environ. Sci. Technol. 26, 889-895.

Quinn, J., Geiger, C., Clausen, C., Brooks, K., Coon, C., O'Hara, S., Krug, T., Major, D., Yoon, W.-S., Gavaskar, A., Holdsworth, T. 2005. Field Demonstration of DNAPL Dehalogenation Using Emulsified Zero-Valent Iron. Environ. Sci. Technol. 39, 1309-1318.

Reinsch, B.C., Forsberg, B., Penn, R.L., Kim, C.S., Lowry, G.V. 2010. Chemical Transformations during Aging of Zerovalent Iron Nanoparticles in the Presence of Common Groundwater Dissolved Constituents. Environ. Sci. Technol. 44, 3455-3461.

Rosenthal, H., Adrian, L., Steiof. M. 2004. Dechlorination of PCE in the presence of Fe^0 enhanced by a mixed culture containing two *Dehalococcoides* strains. Chemosphere 55, 661-669.

Sale, T.C., McWhorter, D.B. 2001. Steady state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields. Water Resour. Res. 37, 393-404.

Saleh, N., Kim, H.-J., Phenrat, T., Matyjaszewski, K., Tilton, R.D., Lowry, G.V. 2008. Ionic Strength and Composition Affect the Mobility of Surface-Modified Fe^0 Nanoparticles in Water-Saturated Sand Columns. Environ. Sci. Technol. 42, 3349-3355.

Saleh, N., Phenrat, T., Sirk, K., Dufour, B., Ok, J., Sarbu, T., Matyjaszewski, K., Tilton, R.D., Lowry, G.V. 2005. Adsorbed Triblock Copolymers Deliver Reactive Iron Nanoparticles to the Oil/Water Interface. Nano Lett. 5, 2489-2494.

Saleh, N., Sirk, K., Liu, Y., Phenrat, T., Dufour, B., Matyjaszewski, K., Tilton, R.D., Lowry, G.V. 2007. Surface Modifications Enhance Nanoiron Transport and NAPL Targeting in Saturated Porous Media. Environ. Eng. Sci. 24, 45-57.

Sarathy, V., Tratnyek, P.G., Nurmi, J.T., Baer, D.R., Amonette, J.E., Chun, C.L., Penn, R.L., Reardon, E.J. 2008. Aging of Iron Nanoparticles in Aqueous Solution: Effects on Structure and Reactivity. J. Phys. Chem. C 112, 2286-2293.

Scherer, M.M., Richter, S., Valentine, R.L., Alvarez, P.J.J. 2000. Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean up. Crit. Rev. Environ. Sci. Technol. 30, 363-411.

Scheutz, C., Broholm, M.M., Durant, N.D., Weeth, E.B., Jørgensen, T.H., Dennis, P., Jacobsen, C.S., Cox, E.E., Chambon, J.C., Bjerg, P.L. 2010. Field Evaluation of Biological Enhanced Reductive Dechlorination of Chloroethenes in Clayey Till. Environ. Sci. Technol. 44, 5134-5141.

Schnarr, M., Truax, C., farquhar, G., Hood, E., Gonullu, T., Stickney, B. 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. J. Contam. Hydrol. 29, 205-224.

Schrick, B., Blough, J.L., Jones, A.D., Mallouk, T.E. 2002. Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles. Chem. Mater. 14, 5140-5147.

Schrick, B., Hydutsky, B.W., Blough, J.L., Mallouk, T.E. 2004. Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater. Chem. Mater. 16, 2187-2193.

Shackelford, C., Sale, T., Liberat, M., 2005 In-Situ Remediation of Chlorinated Solvents using Zero Valent Iron and Clay Mixtures: A Case History. Proceedings from Geo-Frontiers, January 2005, Austin, Texas. Geotech. Sp. 142.

She, H.Y., Sleep, B.E. 1999. Removal of Perchloroethylene from a Layered Soil System by Steam Flushing. Ground Water Monit. Remediat. 19, 70-77.

Siegrist, R.L., Lowe, K.S., Murdoch, L.C., Case, T.L., Pickering, D.A. 1999. In Situ Oxidation by Fracture Emplaced Reactive Solids. J. Environ. Eng. 125, 429-440.

Siegrist, R.L., West, O.R., Morris, M.I., Pickering, D.A., Greene, D.W., Muhr, C.A., Davenport, D.D., Gierke, J.S. 1995. ln Situ Mixed Region Vapor Striming in Low-Permeability Media. 2. Full-Scale Field Experiments. Environ. Sci. Technol. 29, 2198-2207.

Sleep, B.E., McClure, P.D. 2001. Removal of volatile and semivolatile organic contamination from soil by air and steam flushing. J. Contam. Hydrol. 50, 21-40.

Smatlak, C.R., Gossett, J.M. 1996. Comparative Kinetics of Hydrogen Utilization for Reductive Dechlorination of Tetrachloroethene and Methanogenesis in an Anaerobic Enrichment Culture. Environ. Sci. Technol. 30, 2850-2858.

Soga, K., Page, J.W.E., Illangasekare, T.H. 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. J. Hazard. Mater. 110, 13-27.

Song, H., Carraway, E.R. 2005. Reduction of Chlorinated Ethanes by Nanosized Zero-Valent Iron: Kinetics, Pathways, and Effects of Reaction Conditions. Environ. Sci. Technol. 39, 6237-6245.

Song, H., Carraway, E.R. 2006. Reduction of Chlorinated Methanes by Nano-Sized Zero-Valent Iron. Kinetics, Pathways, and Effect of Reaction Conditions. Environ. Eng. Sci. 23, 272-284.

Stroo, H.F., Unger, M., Ward, C.H., Kavanaugh, M.C., Vogel, C., Leeson, A., Marqusee, J.A., Smith, B.P. 2003. Chlorinated Solvent Source Zones. Environ. Sci. Technol. 37, 225-230.

Su, C., Puls, R.W. 1999. Kinetics of Trichloroethene Reduction by Zerovalent Iron and Tin: Pretreatment Effect, Apparent Activation Energy, and Intermediate Products. Environ. Sci. Technol. 33, 163-168.

Taghavy, A., Costanza, J., Pennell, K.D., Abriola, L.M. 2010. Effectiveness of nanoscale zero-valent iron for treatment of a PCE–DNAPL source zone. J. Contam. Hydrol. 118, 128-142.

Tee, Y.-H., Grulke, E., Bhattacharyya, D. 2005. Role of Ni/Fe Nanoparticle Composition on the Degradation of Trichloroethylene from Water. Ind. Eng. Chem. Res. 44, 7062-7070.

Tratnyek, P.G., Johnson, R.L. 2006. Nanotechnologies for environmental cleanup. Nano Today 1, 44-48.

Troldborg, M., Lemming, G., Binning, P.J., Tuxen, N., Bjerg, P.L. 2008. Risk assessment and prioritisation of contaminated sites on the catchment scale. J. Contam. Hydrol. 101, 14-28.

Troldborg, M., Nowak, W., Tuxen, N., Bjerg, P.L., Helmig, R., Binning, P.J. 2010. Uncertainty evaluation of mass discharge estimates from a contaminated site using a fully Bayesian framework. Water Resour. Res. 46, W12552.

US EPA 2004. Cleanup of the Nation's Waste Sites: Markets and Technology trends. Office of Solid Waste and Emergency Response, US Environmental Protection Agency, EPA 542-R-04-015.

US EPA 2008. The Contaminated Site Clean-Up Information (CLU-IN), US Environmental Protection Agency, Washington, DC. Accessed January 15th 2011 on: http://cluin.org/download/remed/nano-site-list.pdf

US EPA 2010. Superfund Remedy Report, 13th edition. Office of Solid Waste and Emergency Response, US Environmental Protection Agency, EPA-542-R-10-004.

Van Valkenburg, M.E., Annable, M.D. 2002. Mobilization and entry of DNAPL pools into finer sand media by cosolvents: two-dimensional chamber studies. J. Contam. Hydrol. 59, 211-230.

VanderKwaak, J.E., Sudicky, E.A. 1996. Dissolution of non-aqueous-phase liquids and aqueous-phase contaminant transport in discretely-fractured porous media. J. Contam. Hydrol. 23, 45-68.

Varadhi, S.N., Gill, H., Liao, K., Blackman, R.A., Wittman, W.K. 2005. Full-Scale Nanoiron Injection for Treatment of Groundwater Contaminated with Chlorinated Hydrocarbons. Proceedings from Natural Gas Technologies Conference, February, 2005, Orlando, Florida.

Wadley, S.L.S., Gillham, R.W., Gui, L. 2005. Remediation of DNAPL Source Zones with Granular Iron: Laboratory and Field Tests. Ground Water 43, 9-18.

Waldemer, R.H., Tratnyek, P.G., Johnson, R.L., Nurmi, J.T. 2007. Oxidation of Chlorinated Ethenes by Heat-Activated Persulfate: Kinetics and Products. Environ. Sci. Technol. 41, 1010-1015.

Walker, R.C., Hofstee, C., Dane, J.H., Hill, W.E. 1998. Surfactant enhanced removal of PCE in a nominally two-dimensional, saturated, stratified porous medium. J. Contam. Hydrol. 34, 17-30.

Wang, C.-B., Zhang, W.-X. 1997. Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs. Environ. Sci. Technol. 31, 2154-2156.

Webb, S.W., Phelan, J.M. 1997. Effect of soil layering on NAPL removal behavior in soil-heated vapor extraction. J. Contam. Hydrol. 27, 285-308.

Weeks, K.R., Bruell, C.J.. Mohanty, N.R. 2000 Use of Fenton's Reagent for the Degradation of TCE in Aqueous Systems and Soil Slurries. Soil Sediment Contam. 9, 331-345.

Wei, Y.-T., Wu, S.-C., Chou, C.-M., Che, C.-H., Tsai, S.-M., Lien, H.-L. 2010. Influence of nanoscale zero-valent iron on geochemical properties of groundwater and vinyl chloride degradation: A field case study. Water Res. 44, 131-140.

Wu, L., Shamsuzzoha, M., Ritchie, S.M.C. 2005. Preparation of cellulose acetate supported zero-valent iron nanoparticles for the dechlorination of trichloroethylene in water.

Xiu, Z., Jin, Z., Li, T., Mahendra, S., Lowry, G.V., Alvarez, P.J.J. 2010. Effects of nano-scale zero-valent iron particles on a mixed culture dechlorinating trichloroethylene. Bioresour. Technol. 101, 1141-1146.

Yang, Y., McCarty, P.L. 2000. Biologically Enhanced Dissolution of Tetrachloroethene DNAPL. Environ. Sci. Technol. 34, 2979-2984.

Yang, Y., McCarty, P.L. 2002. Comparison between Donor Substrates for Biologically Enhanced Tetrachloroethene DNAPL Dissolution. Environ. Sci. Technol. 36, 3400-3404.

Yu, S., Semprini, L. 2009. Enhanced reductive dechlorination of PCE DNAPL with TBOS as a slow-release electron donor. J. Hazard. Mater. 167, 97-104.

Zhang, W.-X., Wang, C.-B., Lien, H.-L. 1998. Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catal. Today 40, 387-395.

Zhu, J., Sykes, J.F. 2004. Simple screening models of NAPL dissolution in the subsurface. J. Contam. Hydrol. 72, 245-258.

9 Papers

I. Grieger, K.D., Fjordbøge, A., Hartmann, N.B., Eriksson, E., Bjerg, P.L., Baun, A. (2010). Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for *in situ* remediation: Risk mitigation or trade-off? J. Contam. Hydrol. 118, 165-183.

II. Fjordbøge, A.S., Olson, M.R., Sale, T.C., Kjeldsen, P. (2011). ZVI-Clay soil mixing – an innovative remediation technology for chlorinated solvents source zones. Manuscript.

III. Fjordbøge, A.S., Riis, C., Christensen, A.G., Kjeldsen, P. (2011). ZVI-Clay remediation of a chlorinated solvent source zone, Skuldelev, Denmark: 1. Site description and source mass reduction. Manuscript to J. Contam. Hydrol.

VI. Fjordbøge, A.S., Lange, I.V., Bjerg, P.L., Binning, P.J., Riis, C., Kjeldsen, P. (2011). ZVI Clay remediation of a chlorinated solvent source zone, Skuldelev, Denmark: 2. Groundwater mass discharge reduction. Manuscript to J. Contam. Hydrol.

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